Comparison of Biofiltration Media in Treating Industrial Stormwater Runoff

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Dedication

This thesis is dedicated to my parents, Patty and Steve Isaacson for their unwavering support, and to my close friends who helped keep me sane through the duration of this project.

Abstract

Biofiltration systems have become one of the most commonly used best management practices in dealing with stormwater runoff. Stormwater runoff is inherently variable, with the contaminants present depending greatly on the land use of the catchment basin. This study characterized the stormwater collected from an industrial site in northeastern Minnesota. It was determined the pollutants of concern for this site are dissolved heavy metals (Aluminum, Copper, Iron) and bacteria.

Different media exhibit different strengths and weaknesses in the removal of pollutants in these biofiltration systems. As a result, there is not a universal combination of media that can adequately treat all stormwater. 18 bio-based media were tested in batch experiments to determine if they possessed any capacity for heavy metal removal. Eight media (APTsorb, bioAPT, biochar, marble, sand, vermiculite, and zeolite) that showed good removal were studied further in downward flowing column experiments. These column experiments determined that all materials demonstrated some capacity for dissolved metal removal with the exception of sand. However, marble performed the best by a significant margin, removing over 10 mg/cm^3 of iron, 4 mg/cm^3 of aluminum, and 2 mg/cm^3 of copper.

The four materials that were determined to have the largest removal capacity for heavy metals (APTsorb, compost, marble, zeolite) were tested in an additional column experiment in which the synthetic stormwater was inoculated with *E. coli*. Marble again performed the best removing 100% of *E. coli* throughout the duration of a 56-hour

continuous flow column experiment. This characterization process provides valuable information on the effectivity and longevity of a variety of media in the design of future biofiltration systems.

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1. Introduction to Stormwater and Stormwater Pollutant Removal Mechanisms

1.1 Stormwater

Urban stormwater, a non-point source pollutant, is a growing concern as rapid urbanization continues, and the number of impermeable surfaces; such as roads, parking lots, and structures steadily increases. The pollutant loading of stormwater runoff is substantial and was identified as a primary contributor for impaired water bodies (approximately 18% of lakes, and 32% of estuaries in the US) (USEPA 2000). Pollutants can accumulate on surfaces during dry days and are subsequently washed into receiving waters during rain events (Brown 2006). Stormwater runoff can contain a variety of pollutants including nutrients, metals, bacteria, and trace organic compounds (Moore 2016, Chandrasena 2017).

The composition of pollutants in stormwater can vary depending on the land use of the catchment basin (Goonetilleke 2005). For example, an agricultural field would likely experience different sources of pollutant deposition relative to a commercial parking lot, and as such would have different pollutants in the stormwater. In an agricultural field the primary source of pollutant deposition would likely come from fertilizers or other soil amendments. The runoff from such areas would be expected to have elevated levels of nutrients such as nitrogen. A study by Ghane et al. in 2016, showed nitrogen loading from fertilized agricultural land was 13 times the loading found in city stormwater. This is contrary to a parking lot, where pollutant deposition likely

comes from the weathering of automobiles. This process can lead to the presence of increased levels of heavy metals and petroleum hydrocarbons (Lui 2015).

This study characterizes the stormwater runoff from a metal foundry in northeastern Minnesota. This is an industrial region, with many sites discharging their stormwater into the nearby St. Louis estuary, which feeds directly into Lake Superior (MPCA 2000). The unique characteristics of Lake Superior make it particularly susceptible to pollutants (MPCA 2000). Taking measures to prevent additional pollutant loading from runoff could help maintain the health of this unique resource. National Pollution Discharge Elimination System (NPDES) permits for these facilities require quarterly monitoring of copper, iron, aluminum, zinc, nitrate, nitrate, chloride, sulfate, and phosphate.

The presence of heavy metals in the stormwater is of concern as this region of Minnesota has a rich industrial history, and there are several foundries and metal fabricators in the region. Metals can be present in particulate, dissolved, or colloidal forms, and can be introduced from automobiles (e.g. corrosion, fluid leaks, wearing of brake pads), buildings (e.g. weathering of paints, decomposition of metal features), and atmospheric deposition (Davis 2003). Metals in aquatic environments are of concern because they can be dissolved in water and subsequently absorbed by aquatic organisms. While some metals such as copper, zinc, iron, and cobalt are micronutrients, and essential to living organisms at low concentrations, they can induce toxic effects at higher concentrations (Stankovic 2014). Additionally, because metals are not degradable in

natural environments there is also a risk of bioaccumulation of metals in the food chain (Tchounwou 2010).

Microbial pollutants are also of concern, as the EPA reports bacteria as a primary cause of surface water quality impairment for 35% of impaired rivers and streams in the United States (USEPA2000). Many pathogens are found in the fecal matter of animals (both wild and domesticated), and a study performed by Mallin et al. (2000), found that as the amount of impervious surface increased in a catchment basin so did the amount of indicator bacteria in the receiving waters (Taylor 2015). These impervious surfaces are typically a sign of human activity, which comes with the associated pet and vermin waste. In humans, direct contact with fecal contaminates can results in adverse health effects such as fever, sore throat, and gastrointestinal illness (Haile et. al 1999). Exposure can occur from swimming or consumption of food (e.g. fish, shellfish, and algae) from contaminated water bodies (Booth 2006). The close proximity of this industrial region to a large body of water makes many of these industrial sites a desirable location for waterfowl. The presence of these birds raises concerns of microbial contaminants being present in the stormwater runoff.

1.2 Biofiltration

The impacts of stormwater pollutants can be mitigated by employing best management practices (BMP) to control the runoff. Currently many natural-based BMPs such as swales, infiltration trenches, rain gardens, and retention/detention ponds are employed. Many of these BMPs do a good job attenuating peak flows, however, they often lack substantial water quality treatment. Biofiltration systems have emerged as a

possibility to address stormwater quantity and improve the quality of the discharged waters within urban catchments (Dietz 2007). The filter media used in these systems includes a combination of soil-based material, organic material, or other soil amendments in order to provide adequate water drainage, pollutant removal, and support for vegetation and microbial communities (Lim 2015). These systems offer a low maintenance, and inexpensive option for both dealing with water quantity and quality.

Research around biofiltration systems tend to be performed in urban, commercial, or agricultural areas as opposed to an industrial setting. As such these systems have been shown to successfully remove particle bound metals and some nutrients, however, they often fail to adequately remove dissolved heavy metals which are a concern in industrial areas (Bernhardt 2012). The removal of these dissolved metals is of particular importance as dissolved metals are more bioavailable than their particulate counterparts (Tchounwou 2012).

From a conceptual standpoint biofiltration should be able to remove the majority of microbial pollutants. Similar to other pollutants, water flows through a filter where bacteria should be removed by a variety of mechanisms. However, in a study by Hunt et al. (2008), only 70% removal of fecal indicator bacteria (FIB) was seen in a field operated sand biofilter. A similar sand filter with vegetation was shown to decrease FIB present in agricultural runoff by 91.3% in a laboratory setting (Rusciano 2007). These are encouraging results and show that there is potential for biofiltration to remove pathogenic bacteria. However, the median concentration of bacteria in industrial stormwater in Minnesota is 9700 MPN/100mL (MPCA 2007). 91% of removal from this median value

fails to reach a concentration appropriate for recreation (126 MPN/100mL) (USEPA 2012). While metal and nutrient removal data by biofiltration media is readily available in the literature, very little work has been done on the ability of various media to remove fecal indicator bacteria (FIB).

1.3 Pollutant Removal Mechanisms

Treatment in these biofiltration cells occurs when the stormwater percolates through the media, and the pollutants are removed by physical, chemical or biological mechanisms (Lim 2015). Physical mechanisms, such as straining (Stevik 2002) or physical adsorption, depend on media characteristics such as particle size distribution and shape (Gunatilake 2015). Straining is a removal mechanism that does not play a role in dissolved metal removal, however, would likely be the primary mechanism by which bacteria removal would occur. Straining occurs when a bacterium or microorganism is larger than the pore space in the media (Pekdeger 1983). This mechanism is dependent on both the physical characteristics (e.g. morphology, particle size, heterogeneity, pore structure) of the media, and the bacteria present in the storm water (Lawrence 1996, Bouwer 1984). An issue that can arise when straining is the primary removal mechanism is the decrease in hydraulic conductivity of the media over time (Schwager 1997). As the pore space is clogged with particles/bacteria the stormwater percolates through the media at a slower rate. The increased hydraulic retention time that comes with the clogging pores has been shown to result in increased levels of fecal coliform removal in a study by Kristiansen (1981). While clogging may have a positive effect on treatment, the MPCA dictates that the drawdown of biofiltration systems must occur within 48 hours (MPCA

2007). As such care must be taken to ensure that clogging isn't severe enough to cross this threshold.

Adsorption is a separation process in which a liquid phase substance becomes bound to the surface of a solid by physical and/or chemical interactions (Kurniawan 2006). The bonding process can result in the capture of heavy metals and bacteria from the stormwater. Physical adsorption tends to result in a weak, reversible bond formed primarily from Van der Waals forces or hydrogen bonding (Tas 2014). The weak strength of this bond makes this an undesirable removal mechanism.

Chemical removal processes, such as chemical adsorption, precipitation, ion-exchange, or complexation are more desirable than physical mechanisms as they often result it stronger bonds being formed with the pollutants. Chemical adsorption results in an irreversible form of adsorption, or adhesion (Mozes 1987). This removal mechanism requires a large amount of energy and is reliant on continuous contact between the pollutant and the surface (Stevik 2004). Adhesion occurs when bacteria form polymer linkages (Garret 2008), or the metals form bonds (often covalent) with the adsorbent material (Holt 2016). While this form of adsorption is desired over the physical, it is much less likely to occur as the energy requirement is significantly larger.

Chemical precipitation is a simple mechanism that results in the formation of an insoluble precipitate of the heavy metal pollutant. While this mechanism would play no role in bacteria removal it is a very commonly employed in wastewater treatment to remove heavy metals (Barakt 2011). The increasing of the pH and/or water hardness leads to the production metal hydroxides and carbonates (Gunatilake 2015). This process,

while effective, could lead to the clogging of the filter as metal precipitates accumulate in the pore space (Aziz 2008).

Unlike chemical precipitation, ion-exchange involves an interaction with the either a functional group or the surface of the particle when there is an easily exchangeable cation present (Uchimiya 2011). This mechanism is common in media that have carboxyl groups on the particle surface. These carboxyl groups readily allow for the exchange of a hydrogen ion and result in a chemical bond with the metal cation (Cohen-Shoel 2002). Additionally, a metal complex can form with functional groups or π electron rich domains present on the particle surface (Li 2017). While chemical processes can lead to removal or inactivation of bacteria, the chemical removal mechanisms in biofiltration systems tends to be reserved for non-microbial pollutants.

Biological removal occurs due to the formation of a biofilm which can promote a variety of removal mechanism. Biofilm formation is likely to occur both on the surface and in the pore space between particles in media (Afrooz 2016). Organic materials tend to promote the production of biofilms; however, biofilm formation can occur on inorganic materials, such as sand, after a longer period of time (Bellamy 1985). The growth of a biofilm has been shown to alter the physio-chemical properties of the porous media, altering roughness, hydrophobicity, and electro kinetic properties on the particle surface (Clement 1996). These changes have been shown to influence the interaction between suspended particulates and filter media (Fontes 1991). Additionally, the biofilm itself can act as an adsorbent/absorbent material for the pollutants in the stormwater (Bellin 1993). Copper and zinc are both micronutrients to microbial growth, and the

presence of biofilm activity increased the removal of these contaminants by 35-50% in acid mine drainage (Orandi 2012).

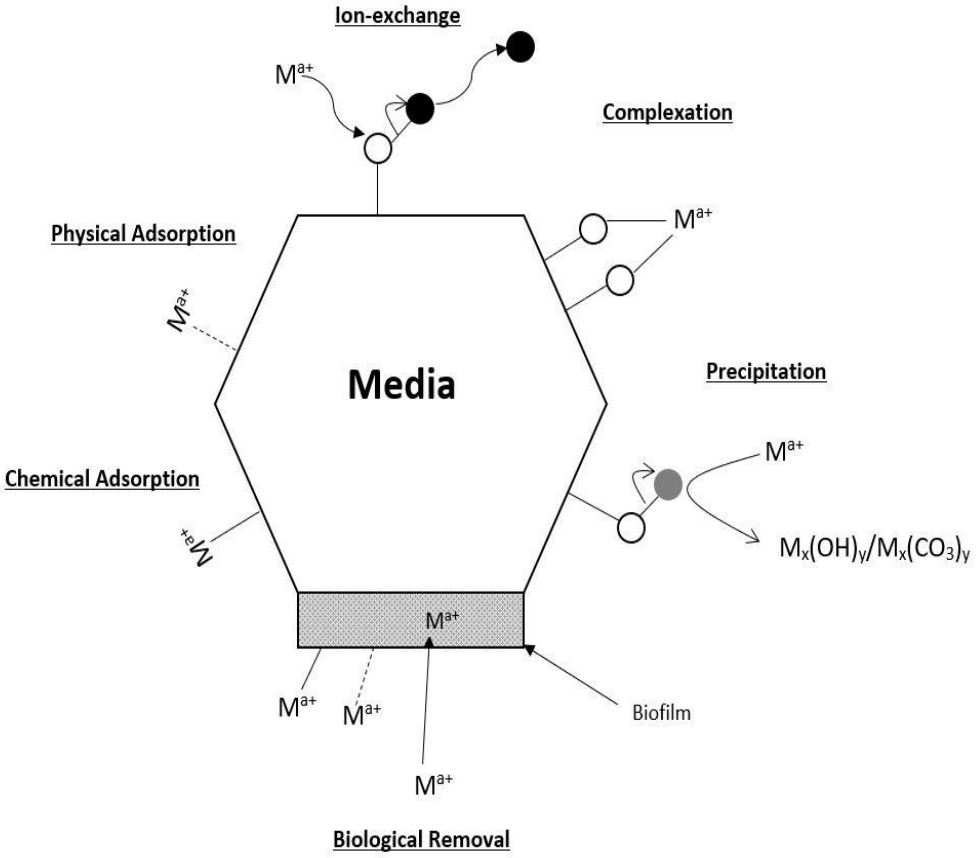

Figure 1. *Biofiltration Removal Mechanisms*

Depicts the removal mechanisms that may be employed by the various media. M represents a heavy metal pollutant, the non-dashed lines represent chemical bonds, dashed lines represent electrostatic bonds, and the filled box represents the biofilm.

The presence of these biofilms has shown inconsistent results in their effect on FIB removal. In a biochar filtration system, the presence of a biofilm decreased the ability for FIB removal (Afrooz 2016) but have shown to consistently increase FIB removal in sand filters (Bellamy 1985).

1.4 Objectives

The objective of this study was to characterize the stormwater runoff from the industrial site and explore potential media for dissolved metal and FIB treatment. The dissolved heavy metal removal capacities of eight media (compost, crushed marble, biochar, vermiculite, sand, and two peat products) were determined by running laboratory-scale bioreactors until breakthrough was observed. Media that were shown to possess the largest metal removal capacities were then tested in their ability to remove FIB during an additional column experiment. This characterization process provides valuable information on the effectivity and longevity of a variety of media in the design of future biofiltration systems for sites with heavy metal and/or bacteria contamination.

2. Stormwater Sampling and Quantitative Analysis of Pollutants

2.1 Introduction

Chapter 2 provides a description of the sampling site, stormwater collection methodologies, and the characterization of stormwater pollutants of concern in the stormwater. Stormwater collection and characterization were conducted during the summer months of 2017 and 2018. The characterization of pollutants in the industrial stormwater will be key information for choosing media that could potentially treat the stormwater.

2.2 Site Description

The study site is an industrial site in northeastern Minnesota that has three stormwater discharge locations at their facility. NPDES permits require the discharged

stormwater to be limited to concentrations of 1.5 mg/L of aluminum, 1.0 mg/L of iron, 0.028 mg/L of copper, and 0.234 mg/L of zinc. The company is currently complying with these limits. They were willing to work with University of Minnesota Duluth to explore bioremediation technologies to reduce the concentrations of their effluent stormwater further.

The stormwater at the facility is collected through a system of drainage ditches and culverts. Each of the stormwater discharges eventually flow to the St. Louis River, through either storm drains or a nearby stream. Sampling is performed at the inflow to the retention pond on the site. The catchment basin for this pond is approximately 3.2 hectares and covered in approximately 35% impervious surface, calculated using a geographic information system (QGIS, version 3.6.3). These surfaces include the road leading into the facility, a parking lot, and a storage yard. The road experiences heavy traffic from semi-trucks. The storage yard provides outdoor storage for many types of metal products. Both areas serve as likely sources of metal deposition. Additionally, during the summer months there is a large presence of wild geese on the site, which contributes to the presence of bacteria in the stormwater runoff.

2.3 Sampling Method

Stormwater collections were conducted using a stationary sampler at the inflow to the retention pond of the facility during the summer months in 2017 and 2018. Prior to a rain event a high-density polyethylene sampling bucket (15L) was placed at the outfall from the culvert leading to the retention pond. The culvert and bucket were covered with a waterproof tarp to prevent any fresh rainfall from entering the sampling bucket.

Because flow was variable and difficult to predict this method allowed for the most pollutant concentrated first flush of runoff to be captured reliably. To prevent any additionally dilution of this first flush rainwater the bucket is collected after it has collected approximately 15L of stormwater. The temperature and pH were measured on-site, and samples were filtered using a 0.22µm PTFE syringe filter and preserved for metal analysis by adding 2% trace metal grade nitric acid or refrigerated at 4°C for anion analysis immediately after collection. 2% nitric acid solution was made by diluting 70% trace grade nitric acid (Fischer) with DI water.

2.4 Laboratory Analysis

2.4.1 **Metal Analysis**

Iron, copper, and aluminum were analyzed using an atomic absorption spectrometer (210GVP Buck Scientific) with a graphite furnace attachment (EPA Methods 202.1, 220.1, 236.1). Wavelengths of 248.3, 309.3, and 324.7nm were used for iron, aluminum, and copper respectively. A deuterium lamp was used for background correction. Background correction is recommended for measured wavelengths below 490nm to reduce false absorbance from any solids present in solution. Iron concentrations were measured against standard solutions between 10-100 µg/L. The iron standard solutions were prepared by dissolving analysis grade Iron (II) Chloride tetra hydrate (Arcos Organics) in 2% trace grade nitric acid. During analysis 5µL of a 5000 mg/L magnesium nitrate hexahydrate (98%, Fischer) solution was added to 15 µL of the sample being analyzed. The magnesium nitrate hexahydrate solution was added to minimize the interference from the matrix and increase the analytical sensitivity. This method provides a detection limit of 2µg/L.

Copper concentrations were measured against standard solutions between 10-100 µg/L. The copper standard solutions were prepared by dissolving analysis grade Copper (II) Chloride dihydrate (Arcos Organics) in 0.1% trace grade metal nitric acid. The dilute 0.1% nitric acid was used since the 2% trace metal grade nitric acid was found to contain enough copper to cause difficulties in staying within the desired concentration range. The 0.1% solution was shown to adequately acidify to samples while minimizing the copper contamination. All copper analyses were performed using 0.1% nitric acid. This method provides a detection limit of 2µg/L

Aluminum concentrations were measured against standard solutions between 20-200 µg/L prepared by dissolving Aluminum Sulfate (99.9%, Arcos Organics) in 2% trace grade nitric acid. This method provides a detection limit of 5µg/L.

For zinc, the Zincon colorimetric method was used which allows for a detection limit of 50.0µg/L (EPA Method 8009). The pH of each sample was adjusted to be between 4 and 5, using 1M trace metal grade nitric acid and 2M sodium hydroxide (Cole-Parmer) as needed. Hach Zincon powder pillows was added to the adjusted samples to induce color change, and the absorbance at 213.9nm was observed using a Hach DR2800 spectrophotometer. Zinc concentrations were measured against standard solutions in the range of 50-3000 µg/L prepared by dissolving analytical grade Zinc Chloride (Arcos Organics) in DI water.

2.4.2 Anion Analysis

Nitrite, nitrate, sulfate, phosphorus, chloride, and bromide analyses were performed using ion-chromatography. A Dionex ICS-1100 Integrated IC system with a Dionex IonPac AS22 column, and an AG22 guard (EPA Method 300.10) was used. The eluent consisted of 4.5 mM Na_2CO_3 and 1.4 mM $NaHCO_3$ and flowed at a rate of 1.2mL/min. Carbonate Buffer was prepared by adding sodium bicarbonate (99.7%, Fischer) and sodium carbonate (99.5%, Fischer) to deionized water. The solution was shaken gently until fully dissolved.

Samples were filtered through a 0.22µm PTFE syringe filter to remove particulates, and a Dionex OnGuard II cartridge M to remove cations to help preserve the longevity of the column. A Dionex 7 anion solution (Thermo Scientific) was used as a standard. Concentrations were determined by integrating the peaks of the anions and comparing against the calibration curve.

2.5 Results/Discussion

Samples during rain events were taken from the site over the past two years (2017 and 2018), the results are summarized in Table 1. The pollutants chosen to be measured for those required under the NPDES permit for the site. Of the 5 anions tested for (Cl^-, NO_3^-, NO_2^-, PO_4^{2-}, SO_4^{2-}) the concentrations present in the runoff were not high enough be viewed as primary concerns. Of the four metals tested (Al, Cu, Fe, Zn), aluminum, iron, and copper were found to be present in concentrations high enough to be of concern.

It was seen that the concentration for zinc was consistently below the detection limit (<50µg/L) of the colorimetric method. In order to quantity the zinc in the stormwater on a parts per billion level, three samples were analyzed using ICP-MS (EPA Method 6020A) which provides a detection limit of 2 µg/L, and the results from this analysis can be seen in Table 2. The ICP-MS confirmed that dissolved zinc was present in the stormwater, but below 10 µg/L. Despite zinc being a component of brake pads, and tires, both of which wear with usage, low concentration of dissolved zinc in the stormwater may be due to the fact that zinc tends to be present in particle bound form in stormwater especially in turbid waters (Maniquiz-Redillas 2014). This suggests that zinc is likely present but is being filtered out prior to analysis. The ability of biofilters to remove particle bound metals is well studied (Davis 2003, Davis 2007), and as such zinc was not further studied in this work.

Unlike zinc, copper tends to be found in a dissolved form regardless the levels of suspended solids in the stormwater (Maniquiz-Redillas 2014). Copper concentrations were found to be under 15 µg/L throughout both sampling seasons, which was approximately half the maximum permitting value of 28 µg/L. The permitting level is set this low due to the acute toxicity of copper in aquatic environments even in low concentrations (USEPA 2016). For these reasons, copper was considered a pollutant of concern for future experiments.

Concentrations of chloride, nitrate, and sulfate were generally constant throughout the sampling seasons. The only sample collected in October of 2017 had higher chloride concentration (~2 fold), which is likely due to the use of a deicing salt as the rain event

happened after the first snow fall of the year. Chloride-based salt was used to aid in the melting of the snow/ice on the roads in the facility (personal communication), and subsequently washed off these surfaces during the rain event. Chloride was found to be present at the highest concentration, however, it was far from the limit of toxicity to aquatic species (200 mg/L) (MPCA 2018). Additionally, chloride is known to be difficult to remove from water without using membrane technologies, and as such considered outside the scope of this project. Nitrate and sulfate were present, but in low enough concentrations that dissolved metal removal was determined to be the primary concern. Phosphate and nitrite were also measured; however, their concentrations were below the detection limits (0.1 mg/L).

***Table 1**. 2017-2018 Stormwater Sampling Results*

2017 samples are averages of 3 rain events, and the 2018 values are averages of 2 rain events. Except for October 2017, and August 2018 both of which only had one rain event. M_T represents total dissolved metal concentration ± standard deviation. NA indicates that only one sample was taken, and therefore no standard deviation was reported.

Sample Date	**$[Fe]_T$ (µg/L)**	**$[Al]_T$ (µg/L)**	**$[Cu]_T$ (µg/L)**	**$[Cl^-]$ (mg/L)**	**$[NO_3^-]$ (mg/L)**	**$[SO_4^{2-}]$ (mg/L)**
	2017					
June	150± 21	150± 18	6.0± 1.1	6.3± 0.82	0.19± 0.098	0.64± 0.42
July	170± 21	210± 20	8.0± 0.8	6.0± 0.61	0.26± 0.12	0.59± 0.15
August	930± 44	720± 45	13± 1.1	6.9± 1.2	0.23± 0.08	0.61± 0.29
September	870± 45	740± 42	14± 1.2	6.8± 1.3	0.29 ± 0.09	0.65± 0.22
October	810(NA)	710(NA)	14(NA)	17(NA)	0.20(NA)	0.63(NA)
	2018					
June	120± 21	110± 20	8.2± 1.2	6.5± 0.3	0.18± 0.07	0.64± 0.11
July	170± 25	210± 17	7.1± 0.7	6.6± 0.4	0.19± 0.11	0.63± 0.19
August	420(NA)	3300(NA)	15(NA)	6.6(NA)	0.23(NA)	0.66(NA)
September	140± 14	140± 11	6.0± 0.2	6.8± 0.6	0.17± 0.08	0.63± 0.14

The levels of iron and aluminum increased with the summer months in 2017 and 2018, and aluminum even reached to the NPDES limits in August of 2018. Iron and aluminum are the most dominant contaminants in the stormwater, and the concentrations seemed to fluctuate based on weather pattern and facility activities. In terms of weather patterns, both the frequency and intensities of rain events can play a role in the pollutant loading. Pollutants accumulate on surfaces during dry days from a variety of sources and are washed off those surfaces during rain events. This means that an abnormal lack of rain events or the presence of only lower intensity events could lead to a higher concentration of pollutants in the runoff during a large or intense rain event. In August of 2018 there was only one rain event that resulted in flow into the sampler. This event came after 22 days of no flow. For reference August of 2017 had no more than 7 days without flow through the culvert. This could potentially explain the spike in the metal concentrations during this period.

The three-month period of increased concentrations in the metals seen in 2017 is likely not due to the weather patterns as there were no periods of extended antecedent dry days. This points to a change in the activity or usage of the site as the cause of the increase. One possibility could be that the large bay doors of the facility are left open more frequently during the summer months. This facility uses metals heavily in their plant processes and it's possible that dust particles with bound metals may have been deposited outside more frequently during these months. Another possibility could be the plant had an unusually high demand for product during these three months, which

involved additional storage of metal product in the storage lot and increased industrial traffic. Or a final possibility could be that the asphalt parking lot and road were resurfaced in July of 2017. Although no literature could be found on the leaching potential of iron and aluminum from asphalt it's feasible that this new layer of asphalt resulted in some metal leaching.

Although not reported, the coliform and *E. coli* levels were tested in one of the sampling events (September 2018) to evaluate microbial water quality. The sample had >2400 MPN/100mL for *E. coli*. Due to the risk associated with bacteria and the high concentration observed, FIB is considered to be a secondary pollutant of concern for future experiments.

Table 2. *2017 Stormwater Samples (ICP-MS).*

Stormwater samples from the 2017 sampling season analyzed via ICP-MC. Only one sample from each month was tested.

Sample Date (2017)	[Fe] (µg/l)	[Al] (µg/L)	[Cu] (µg/L)	[Zn] (µg/L)
July	164	224	7	2
August	942	715	10	7
September	863	746	6	3

2.6 Conclusions

The primary dissolved pollutants of concern for this site are aluminum, copper, and iron. Particulate metals were considered outside the scope of this experiment, as many filter media have shown excellent ability in removal from stormwater (Davis 2009). In terms of anions present in the stormwater, the concentrations found in the water

were relatively low on all accounts. FIB was shown to be present and is considered a secondary pollutant of concern, however, not enough data was collected to report a value.

3. Investigation of Heavy Metal and Anion Removal from Stormwater Using Various Media in Batch Experiments

3.1 Introduction

Chapter 3 describes the evaluation of 18 media for the removal of primary contaminants using batch experiments. The batch experiments were conducted with the stormwater collected from the study site. The 18 media selected were chosen based primarily on literature review, and secondarily on cost and availability. Many of the media chosen had shown in previous studies the ability to remove a pollutant of concern from either wastewater (Kurniawan 2006), stormwater (Davis 2009), acid mine drainage (Orandi 2012), or landfill leachate (Sizirici 2018). Media that showed good heavy metal removal and/or minimal anion leaching were chosen for additional experimentation in flow through columns.

3.2 Experimental Design

Batch experiments were performed in 250 mL acid-washed polypropylene beakers, as shown in Figure 2. Each beaker had 200mL of stormwater added to 5 grams of media. With an exception being vermiculite and perlite, where only 2 grams of media was added due to the extremely low density of the materials. The stormwater was filtered through a colander on site to remove any large debris, such as sticks or leaves, and was then added to the media within 1 hour of collection. The beakers were covered with parafilm to prevent contamination and evaporation. The samples were allowed to sit for

24 hours at 21°C. A total of three sets of batch experiments were run, and each material was run in duplicate for each batch experiment. The stormwater used for each of the batch experiments is detailed in Table 3. The first batch experiment used stormwater collected in July of 2017, the second two used stormwater collected from two different rain events in August of 2017.

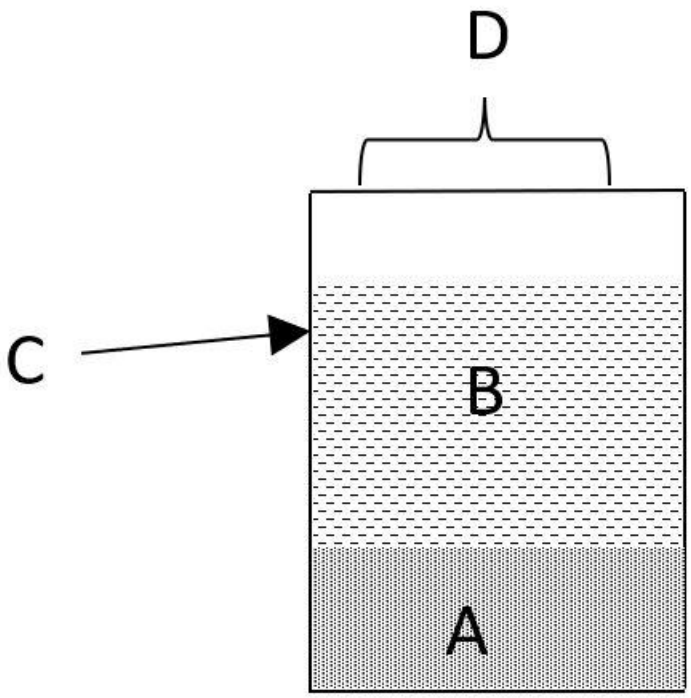

Figure 2. *Diagram of the batch experimental setup.*

A diagram of the batch experiment where A: 5gram of media, B: 200mL of collected stormwater, C: 250mL polypropylene beaker, D: parafilm covering

After 24 hours the pH of the beakers was measured, and samples were taken and filtered using a 0.22µm PTFE syringe filter. 24-hours was chosen as the residence time to allow for equilibrium to be reached in the beaker. This residence time wouldn't be feasible in a biofilter; however, it was used to counteract the lack of flow through the

media to provide a better idea of the capacity of each material. Two samples were taken from each beaker, once at the surface and another near the media at the bottom of the beaker to ensure that the concentration was equal throughout the beaker. These samples were then analyzed for dissolved metals and major anions denoted previously.

Table 3. *Initial Batch Concentrations.*

The initial concentrations of the pollutants present in the stormwater used for the batch experiments.

Batch Experiment	**[Fe] (µg/L)**	**[Al] (µg/L)**	**[Cu] (µg/L)**	**[Cl] (mg/L)**	**[NO_3] (mg/L)**	**[SO_4] (mg/L)**
1	135	156	3	6.467	0.201	0.678
2	880	690	6	5.645	0.274	0.563
3	950	740	15	6.912	0.242	0.5978

3.3 Media Selection

Organic Materials

3.3.1 APTsorb/BioAPT

APTsorb and BioAPT are two biofiltration media derived from peat (American Peat Technologies LLC). Peat is a natural product that is formed by partially decomposed plant matter (Moore 2006). Peat tends to be complex in chemical structure and has several oxygenated functional groups that can potentially be involved with ion-exchange or complexation with the metal cations in the stormwater (Gupta 2009). Peat is an appealing biofiltration amendment as it is low in cost, locally available, and is able to support vegetation (Biesboer 2004). A study by Kasiuliene et al. (2018), showed that peat was able to remove 88% of copper and 46% of zinc from aqueous solutions.

APTsorb and BioAPT are both hardened granulated peat products which maximizes their surface area and allows for them to be easily wet. APTsorb was designed specifically to enhance metal removal from waters, whereas BioAPT was developed as a microbial carrier to be used in agriculture.

3.3.2 Biochar

Biochar is a carbon rich material produced by the thermal decomposition of a biomass in the absence of oxygen (Lehmann 2015). This process produces a material high in surface area and bio-oils (Lehmann 2015). These characteristics of biochar have been shown to remove 70-80% of copper (Pisciteel 2018), and 83-100% of FIB (Mohanty 2014) in synthetic stormwaters. The physical and chemical attributes of biochar can vary greatly depending on the type of biomass used and the pyrolysis temperature (Antal 2003, Gaskin 2008). This study is used a hardwood biochar pyrolyzed at 600°C, and as such the results reported are only reflective of biochar produced under these conditions.

3.3.3 Charcoal

Charcoal was chosen to be tested to see how much of an effect the lack of oxygen had on the effectivity of biochar during pyrolysis. The charcoal was produced in a muffle furnace using hardwood woodchips at 600°C for 24 hours.

3.3.4 Compost

Compost is a cheap, widely available material that is commonly used in these biofiltration systems as a top layer to help assist with vegetation growth (Lim 2015). Compost is formed by the humification process of an organic material (mushrooms in the

case of this media). This humification process has been shown to strongly increase the metal sorption ability of compost (Jang 2005). Several studies have demonstrated the ability of composted materials to immobilize copper and zinc in heavy metal contaminated soils (Mule 2000, Huang 2016). The humification process causes compost to be rich in nutrients, and microorganisms, both which aid in vegetation growth. However, this can also potentially lead to leaching of nutrients (Iqbal 2015) and microorganisms (Mohanty 2014) into the effluent. This study has determined the removal capacity of compost to provide insight on if the removal ability can offset the possibility of leaching.

3.3.5 Gravel

Gravel was chosen because it is often used in biofiltration design to assist in hydraulic conductivity around the underdrain of the system. In a recent study by Sizirici et al. (2018) they showed that gravel was able to remove between 27-98% of metals from landfill leachate. This study aims to determine if gravel will show the same metal removal ability in stormwater.

3.3.6 Fiber Grow Pellet

The “Fiber Grow” pellets are a coconut coir biodegradable product designed to absorb and retain moisture in soils. Similar to compost, coconut coir contains a litany of functional groups that could promote the process of ion-exchange with the metals in the stormwater (Sud 2008). A study by Lim et al. (2015) showed that coconut coir was able to remove up to 90% of zinc and 74% of copper from a synthetic stormwater solution. While Fiber Grow is a commercial soil amendment, coconut coir itself is considered a

waste product. A waste product that displays desirable hydraulic properties and a capacity for metal removal makes this an attractive media.

3.3.7 Mulch

Mulch is common material used as a topping layer in bioretention systems to help prevent erosion and excessive drying of the media (Davis 2001). Mass balances done on these bioretention systems have shown that the top layer of mulch accounted for the majority of copper and zinc capture in these systems (Muthanna 2007, Jang 2005). The mulch used in this experiment is a commercial Cyprus blend.

3.3.8 Orchid Mix

The orchid mix is a commercial product consisting of conifer bark and charcoal and is meant to enhance moisture retention in soils. This media was selected due in part to the low cost, but moisture retention could be a positive attribute of a biofiltration media. This is due to higher retention times often promoting pollutant removal. Additionally, the presence of a wood material provides a carbon source that could enhance the presence of nitrogen fixing bacteria as seen in woodchip bioreactors (Hoover 2016).

3.3.9 Pine bark

Pine bark has shown conflicting results on its efficacy in water treatment. A study done by Nehrenheim et al. (2005) showed that between 20-90% of Zinc and Copper was removed from landfill leachate under a variety of conditions. However, Genc-Fuhrnman et al. (2007) suggested that pine bark may not be suitable for adsorption with heavy

metals in stormwater. Both could be correct as the chemistry is likely vastly different between landfill leachate and typical stormwater runoff. The media was selected despite the unsettled nature of the literature because of it is low cost and the success of similar wood-based media in fostering nitrogen fixing bacteria.

3.3.10 Topsoil

Topsoil was selected as a media because it is a cheap, and a commonly used material in construction of many best management practices for stormwater (rain gardens, swales, etc.). Sand filters amended with 20% topsoil saw a significant increase in copper removal (Blecken 2010). This could likely be attributed to copper's strong affinity for organic matter (Ponizovsky 2006). The organic materials in the topsoil may have the ability to complex with the other pollutants of concern.

3.3.11 Vermiculite

Vermiculite is a hydrous phyllosilicate mineral often used for insulation, composite cements, or horticulture (Abollino 2008, Bergaya 2006). Vermiculite has been shown to be a good adsorbent and has a high surface area both of which are desirable filter media traits (Lee 2011). In a study by Fonseca et al. (2005) it was shown that vermiculite was able to successfully remove copper from an aqueous solution.

3.3.12 Woodchips

The woodchips used for this study were white cedar chips purchased locally. Woodchips were chosen because it is a cheap media that have been shown to reduce nitrate loading in agricultural runoff (Hoover 2016). The woodchips act as a source of

organic carbon that can be used by microbes under anaerobic conditions (Hoover 2016). While nitrate is not a primary concern for the runoff at this site, woodchips have also shown to have the ability to remove copper from stormwater (Ashoori 2019), and 75-83% of *E. coli and Salmonella* bacteria in pilot scale bioreactors treating agricultural runoff.

Inorganic Materials

3.3.13 Marble

The marble used in this study was in the form of marble chips (typically used for landscaping) that were pulverized down to a smaller non-uniform particle size. This was done to provide more surface area for the material. Marble was chosen because in previous studies calcite, a major component of marble, has shown the ability to remove 25% of Iron, 93% of aluminum, 5% of zinc, and 95% of copper from acid mine drainage (Rötting 2008, Xu 1997). Marble is more expensive than most of the other media tested, however, even in small amount could be used to help enhance removal.

3.3.14 Perlite

Perlite is an artificial soil material made from volcanic glass, often formed by the hydration of obsidian. It's a lightweight porous material that has excellent drainage characteristics, both of which are desirable in the biofiltration environment (Gironas 2008). Most studies done involving perlite include it only in combination with other media and have seen encouraging results in removal of both nutrients and heavy metals (Bratieres 2008, Hatt 2009, Feng 2012). This study aims to determine if perlite may contribute metal removal in these systems or just assists in hydraulic conductivity.

3.3.15 Sand

Sand was included as a control because it's an inexpensive, widely available, and a well-studied media. In terms of the pollutant removal, sand has shown mixed results in removal of dissolved metals, removing between 5-43% for copper and 43-58% for zinc (Reddy 2014). Additionally, slow sand filters have shown an ability to remove 80-100% of FIB from contaminated waters (Yogafanny 2014, Elliot 2008). Due to the low cost of sand it is commonly used in biofilter designs, often in conjuncture with other media. Comparing an industry standard with other media was deemed appropriate as a control.

3.3.16 Steel wool

Extra fine steel wool was used for this study and was chosen as a material of interest because it is often added to sand filters to aid in phosphorus removal. In a study conducted by Erickson et al. (2007), sand columns amended with 2% steel wool showed an increase of 25-99% phosphorus removal. These so called "Minnesota Filters" contain between 5-8% iron content and are widely employed across the country (MPCA 2017). This study looks to determine if metal removal or leaching may occur from the usage of this media.

3.3.17 Zeolite

Zeolites are microporous, aluminosilicate materials formed in basaltic rocks that are subjected to moderate geological pressure (Reddy 2014). The negative charge, and porous structure of zeolite accommodates a wide range of cations such as calcium, sodium, potassium, and magnesium (Erdem 2004). These cations are loosely bound to the surface of the zeolite and can readily exchange with cations in aqueous solutions

(Kesraoui-Ouki 1994). The high surface area and chemical properties make zeolite a popular ion-exchange resin in industry. In principle, this same mechanism could be used to remove metal cations from stormwater.

The zeolite used in this experiment was obtained from Bear River Zeolite in Preston, ID. This zeolite is 90-95% clinoptilolite, which has been shown to have a high affinity for copper and zinc cations (Curkovic 1997). The zeolite was rinsed with DI water and dried prior to usage in all experiments. The first batch experiment used a rinsed, and an unrinsed zeolite. The unrinsed zeolite saw a 42% increase in aluminum, whereas the rinsed zeolite removed 58%.

3.4 Results/Discussion

The batch experiment was designed to determine which media should be tested further in laboratory scale column experiments. Figure 3 shows the removal percentage of dissolved copper, iron and aluminum by each of the 18 media in 24 hours. Metal removal was the primary objective of this study; however, it was also important to observe if the materials had any leaching of anions as well. Figure 4 shows the change in anion concentration in the stormwater after being exposed to each media in the batch experiment. These two figures were used to evaluate the performance of each of the media.

Compost showed a concerning amount of leaching of nitrate, chloride, and sulfate into the stormwater. This is viewed as a concern as increased levels of these contaminants can cause oxygen depletion, eutrophication, and species stress on receiving bodies (Davis

1993). Despite the leaching concerns, compost is the most commonly used organic material in biofiltration due to it its ability to improve infiltration, reduce erosion and support plant growth (Maurer 2009, Pitt 1999). Additionally, compost performed best in metal removal out of any of the media tested removing over 90% of all three metals.

BioAPT also showed a leaching of chloride, nitrate, and sulfate but to a much lesser degree than compost. However, based on the American Peat Technologies usage guidelines, their products are to be rinsed with five bed loads of water before usage to prevent leaching of nutrients into the soil. This was something that was neglected in the batch experiments and would explain the small leaching that occurred. In terms of metal removal BioAPT showed 39% aluminum, 43% iron, and 100% copper removal.

The steel wool, fiber grow pellet, charcoal, and orchid mix were the only materials that displayed some degree of metal leaching into the stormwater. It was unsurprising that steel wool leached iron into the stormwater as after 24 hours the steel wool exhibited visible oxidation on the surface. This the primary reason that the MPCA dictates a maximum of 8% steel wool can be used in biofiltration systems (MPCA 2019). The leaching of copper was unexpected as copper tends to only be present in a steel as a residual element. However, due to the very low concentration of copper in the stormwater originally, this would only require between 1-4 µg of leaching to occur from the steel wool.

The aluminum leaching from the charcoal can potentially be explained in a study by Chandrasekaran et al (2012). In this study it was shown that aluminum accounted for up to 1% of the dry weight of ash formed by hardwood woodchips. Figure 3 shows

leaching of 23% at the highest concentration of aluminum in the collected stormwater (740µg/L). This would require only 42.5 µg of aluminum to be leached. Providing the 1% aluminum content value hold true in the charcoal used for this experiment, that would require under 0.1% of the aluminum content on to be leached from the charcoal. This same reasoning could be applied to the orchid mix, as it consists of charcoal/woodchip mix.

Iron is a micronutrient for plants, and as such the leaching displayed by the Fiber Grow pellet could be by design (Brown 1972). The iron content of soil is typically between 1-5% by weight (Irmak 2008). The majority of this iron is in the form of oxides or hydroxides, neither of which is readily available for plant use (Romheld 1987). To prevent iron deficiency and promote plant growth (as Fiber Grow is designed to do) many soil amendments are designed to enhance the available iron content in soil.

The wood materials (pine bark, woodchips, and mulch) all performed similarly removing nearly all the copper but showed very little iron or aluminum removal. However, all three materials did show a 10-20% decrease in nitrate in the stormwater.

Perlite, sand, and gravel all provided no copper removal, a minimal amount of aluminum (< 20%), and iron (< 9%) removal, and showed no effect on the anions. This indicates that these materials are typically only used in biofiltration systems as a cheap way to increase hydraulic conductivity, and assist in mechanical based removal (straining, adsorption, etc.).

Selection of materials for further investigation was dependent of the ability to remove metals from the stormwater. APTsorb, BioAPT, biochar, marble, vermiculite, and zeolite all performed very well by removing 40% or more of all the metals tested, and showed no anion leaching concerns. All five of these materials were chosen to be studied further in the column experiments. Any metal leaching (charcoal, fiber grow pellet, steel wool) removed materials from consideration. Removal of iron and aluminum played a larger role in which materials were studied further due to the higher concentrations of these contaminants present in the stormwater relative to copper (< 15µg/L). As such materials that removed only copper from stormwater (mulch, pine bark, woodchips) were removed from consideration as well. Despite nutrient leaching concerns with compost, it performed the best in metal removal, and is a very commonly used material in biofilter designs and as such was studied further. Finally, due to its prevalence in biofilter design sand was studied further despite low removal rates as a control.

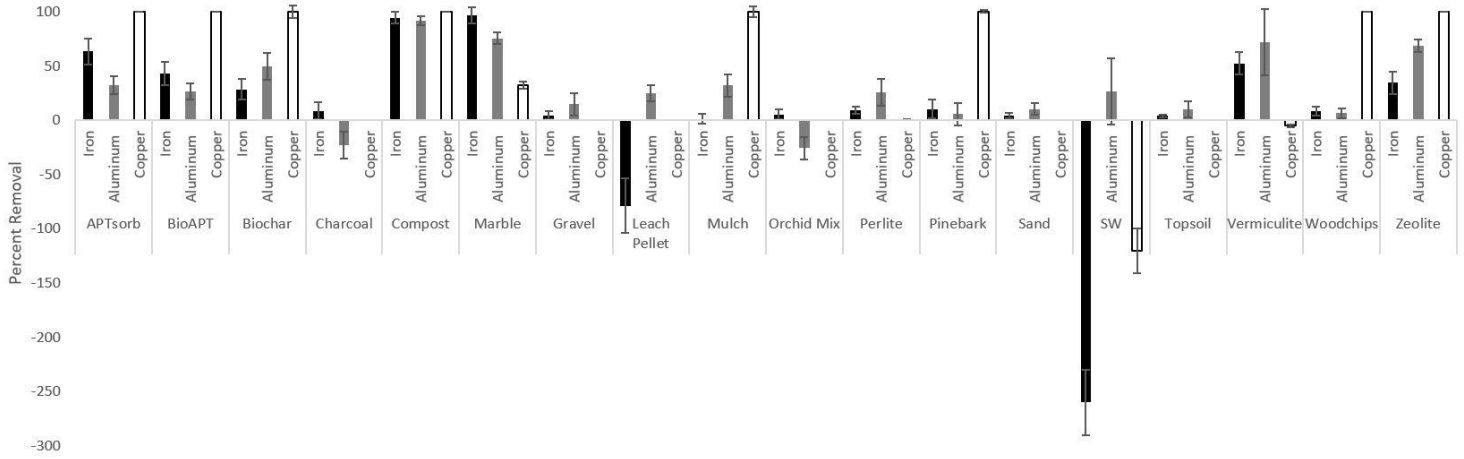

Figure 3*. Percent of metal removed for each media tested in batch experiment.*

The values reported are an average (± standard deviation) removal over the three batch experiments.

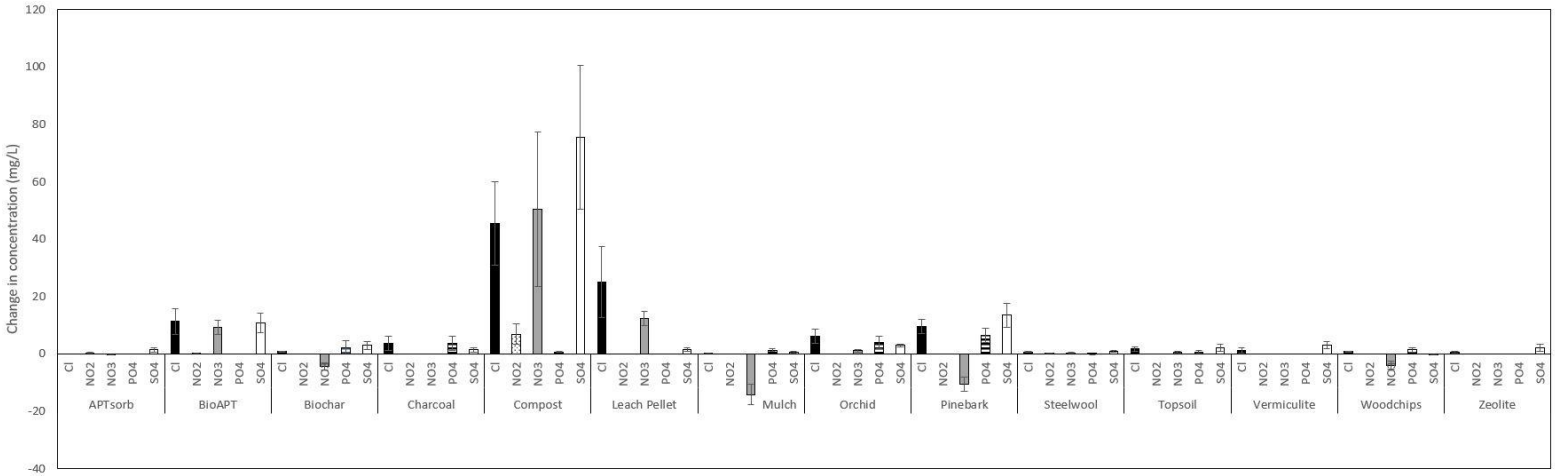

Figure 4. *Average change in concentration of each of the anions tested for in the batch experiment.*

The values reported are an average (± standard deviation) change in concentration of each of the anions over the three batch experiments.

3.6 Conclusions

The batch experiment acted as a screening process to determine media that should be examined further in a column experiment. Seven media (APTsorb, BioAPT, biochar, compost, marble, vermiculite, zeolite) were chosen based on their ability to remove iron, aluminum, and copper from the stormwater. Sand was also selected; however, it is being used as a form of a control as it saw no significant removal of heavy metals. Of these media only compost saw any concerns with leaching of anions into the stormwater. None of the materials selected were seen to have any significant removal of anions from the stormwater.

4. Metal Removal Capacity of Various Media from Stormwater

4.1 Introduction

Chapter 4 presents removal capacities of the selected media that showed good performance in the batch experiments for dissolved metal removal using flow-through columns. Downward flow-through column experiments were run to better simulate a biofiltration system. A synthetic stormwater was used instead of collected stormwater as rainfall is sporadic (and non-existent in the winter). The columns are run until no more metal is being removed in the effluent. Breakthrough curves are generated and analyzed to determine the removal capacity of aluminum, copper, and iron by each of the media.

4.2 Experimental Design

The columns were constructed of glass, each measuring 1.5cm in diameter, 15cm in length, and have an internal volume of 0.136 L (Bio-Rad Econo-Columns). A porous polymer bed with a frit size of 30µm is present at the bottom of each column. A multichannel peristaltic pump (Cole Parmer) was used to pump a synthetic stormwater through the media. Each media was sieved to a particle size between 0.450-0.850 mm, and 5.3 cm^3 was loaded into each column and gently tamped down using a glass rod to assist in the packing. A synthetic stormwater, as described in Table 4 was used for all column experiments.

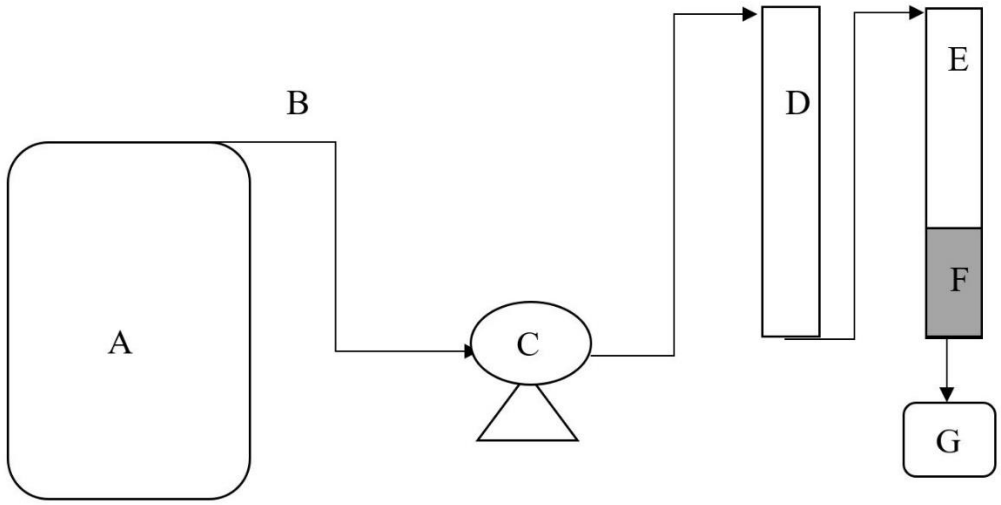

Figure 5. *Metal Capacity Experimental Schematic*

A schematic showing the experimental setup of the metal capacity experiment. Several columns draw from the same reservoir, however, use their individual tubing to do so. A: 15L high density polyethylene reservoir. B: Platinum cured silicone tubing. C: Peristaltic Pump. D: Pre-filter column. E: Media Column. F: Media. G: Polypropylene centrifuge tubes

Synthetic stormwater was prepared by adding the materials listed in Table 4 to DI water. Trace metal grade nitric acid and sodium hydroxide are used to adjust the pH of the synthetic stormwater to be within the desired range. The dissolved metal concentrations in the synthetic stormwater was approximately 10 times greater than the observed values for iron and aluminum, and 150 times the observed value for copper. The increased concentrations allowed for the breakthrough point of each media to be reached within a reasonable amount of time. Subsequently, the pH was set to 5.0, which was lower than observed at the sampling site (pH=6.3) to ensure that the majority of the metals added were dissolved.

Table 4. *Synthetic stormwater contaminant concentration and source.*

Pollutant	Median (min, max)	Source
Iron (µg/L)	1575 (1200, 1850)	$FeCl_2$
Copper (µg/L)	1700 (1500,2000)	$CuCl_2$
Aluminum (µg/L)	1750 (1400,2000)	$Al_2(SO_4)_3$
pH	5.0 ±0.2	

The synthetic stormwater was pumped at a flow rate of 21.3±3 mL/hour. The stormwater flowed through a pre-filter column to ensure that only dissolved metals are being pumped into the media column. This was done because a portion of the metals precipitated out of solution at the chosen pH of the synthetic stormwater. Pumping was continuous through the column and continued until breakthrough was observed. Effluent from the media columns was sampled every bed load (~5.3mL) for the first 100mL, and then every 100-200mL until breakthrough. The effluent of the pre-filter columns was

collected every 1L to ensure that the concentrations entering the media columns remained constant. Samples were collected in polypropylene test tubes and immediately preserved using 2% (for iron and aluminum) or 0.1% (for copper) trace metal grade nitric acid. Samples were analyzed for metal content as described in section 2.3.1.

4.3 Breakthrough Curve Analysis

Figures 6 and 7 show two examples of the breakthrough curves that were generated for each of the column experiments. An error function was used as a regression curve and fit to the data (Equation 1) where $C_{regression}$ represents concentration and is expressed in µg/L, and V_i represents the flow through volume in L at a given sampling point. The parameters (a,b,c) were optimized by minimizing the root mean square error values (RMSE) (Equation 2) between the concentration calculated by Equation 1 and the measured concentration ($C_{observed}$) at each sampling points.

Equation 1. *Error function regression curve*

$$C_{regression} = a \times erf((V_i + b)/c)$$

Equation 2. *Root mean square error equation*

$$RMSE = \sum_{0}^{V_{total}} \sqrt{(C_{regression} - C_{observed})^2}$$

Equation 3. *Metal capacity equation*

$$Capacity = C_{initial} * V_{total} - \int_0^{V_{total}} F(x)dV$$

Equation 3 provides an estimate for *Capacity*, which is the amount of metal removed by the media throughout the experiment. Integrating the error function regression curve, denoted by *F(x)* in Equation 3, with respect to *V* gives an approximation of the amount of metal that passed through the media during the run prior to the end of the experiment. By subtracting the pass-through value from the total amount of metal that passed through the system the removal capacity can be estimated. The total amount of metal that passed through the system can be determined by multiplying the influent concentration ($C_{initial}$) by the total volume that flowed through the system (V_{total}). This analysis process is important for materials such as zeolite (Figure 7) that display a slower logarithmic breakthrough as opposed to marble (Figure 6) where breakthrough occurs very rapidly.

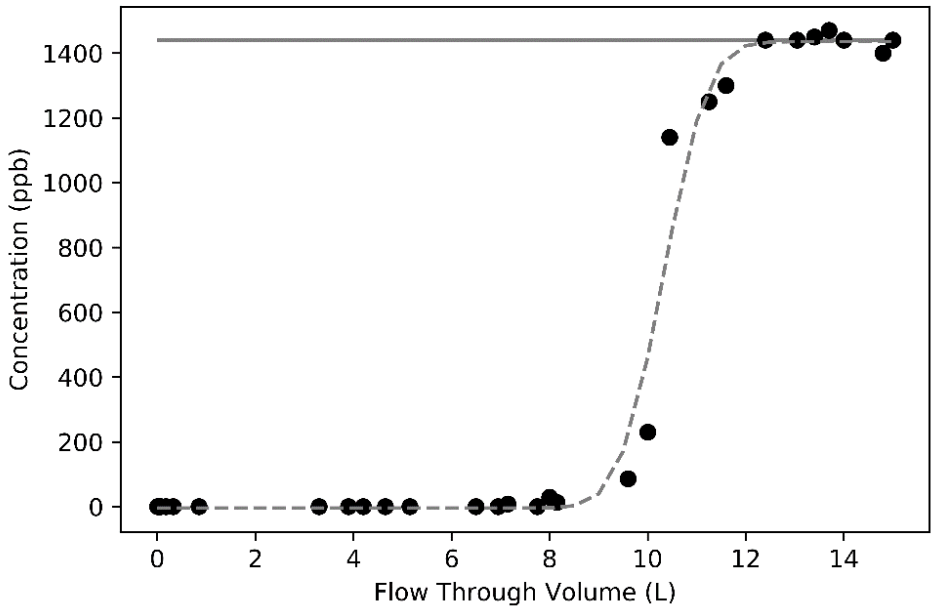

Figure 6. *Aluminum breakthrough curve for marble*

Breakthrough curve depicting the effluent concentration of aluminum after flowing through a marble column. The regression curve generated in python is represented by the dashed lines. The influent concentration of the aluminum is represented by the solid line.

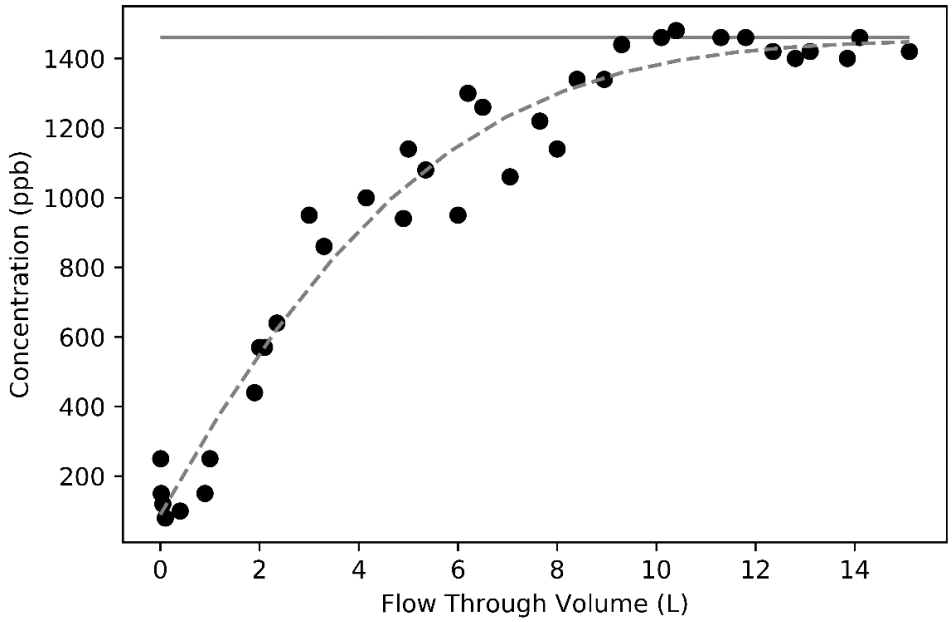

Figure 7. *Iron breakthrough curve for zeolite*

Breakthrough curve depicting the effluent concentration of iron after flowing through a zeolite column. The regression curve generated in python is represented by the dashed lines. The influent concentration of the aluminum is represented by the solid line.

4.4 Results/Discussion

Breakthrough was observed for each of the media, and the curves were used as described previously to generate the results shown in Figure 8. This figure is comprised of the average results of the three columns run for each media and normalizes their removal capacity on a cubic centimeter basis. This was done to account for the organic materials which tended to expand when wetted. Volume was chosen as the basis instead of mass because the design of biofiltration systems are more likely to be dependent on the volume of the system rather than the mass.

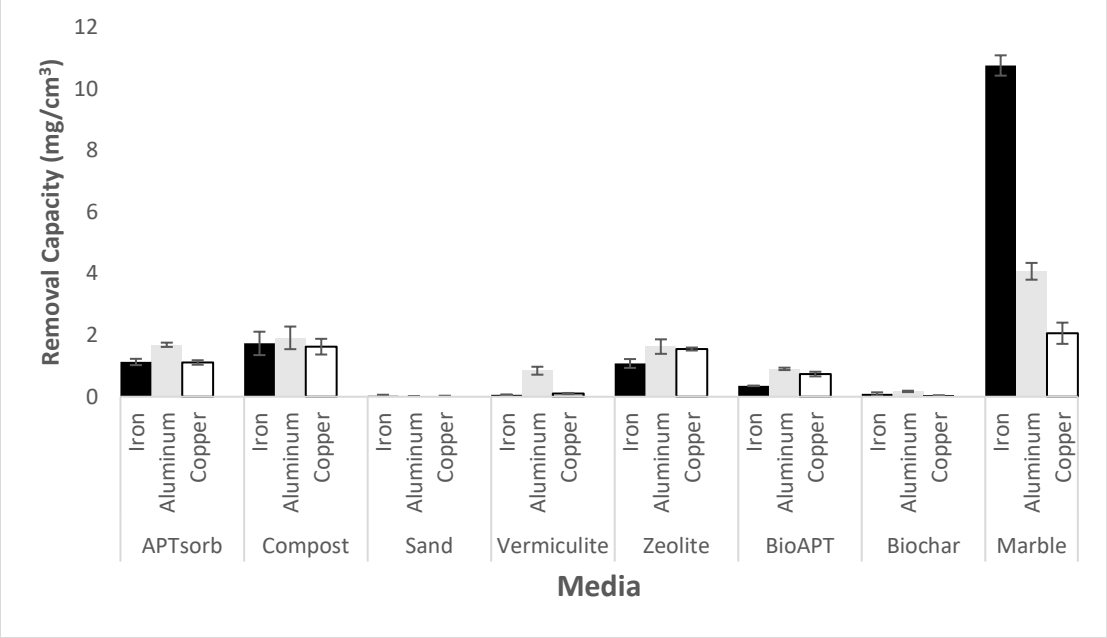

Figure 8. *Media removal capacity of dissolved metals*

Average (mean ± standard deviation) removal capacity of each metal for the media tested in the column experiment (n=3 runs for each) normalized to a bulk volume.

It is important to note that organic materials tend to promote the production of microbial communities known as biofilms. However, outside of marble, all of the column experiments were completed within 20 days. Breakthrough was observed in all columns, however, in a natural environment the system would not undergo constant flow. As a result, the timescale of this experiment is extremely compressed and would not have allowed adequate time for the potential establishment of a biofilm that could be seen in a natural system. Biofilm growth in bioretention cells is variable, and depends greatly on the media, and the stormwater being treated. In a study by Moheimani et al. (2012) it was shown that these biofilms can assist in metal removal, however, they tend to take five or more weeks to establish. This indicates that the mechanisms being observed in this study are limited to the mechanical and chemical varieties. As a result, the removal capacities

reported in Figure 8 of the organic materials (compost, biochar, peats) may be underestimated.

Additionally, the difference in these breakthrough curves can provide insight into the removal mechanism of each of these media. For example, the sigmoidal shape displayed by Figure 6 suggests that the mechanism of removal is based heavily on available surface sites. Whereas Figure 7, may suggest that another, non-surface area dominated mechanism may be occurring.

4.3.1 Marble

Figure 8 shows that crushed marble performed far better than any of the other media tested, removing 10.8 ± 0.334, 4.07 ± 0.273, and 2.06 ± 0.345 mg/cm^3 for iron, aluminum, and copper respectively. The breakthrough point for iron was never reached after allowing the columns to run for 73 days. The iron removal capacity reported is the average amount that was removed before ending the experiment. A likely explanation for the successful removal of iron is that marble causes an increase in the pH of the synthetic stormwater. The pH of the effluent from the marble columns was approximately 8, whereas effluent pH of other media was in the range of 4.5-7. This increased pH is likely due to the high calcium carbonate content in marble. The high pH results in precipitation of the dissolved metals in the form of hydroxides and carbonates. This precipitation process can be seen visually for the iron as the white marble turned a reddish orange color over the course of the experiment, indicating iron carbonate deposition.

Despite being less effective at removal of copper and aluminum relative to iron, the marble still performed better than the other media. Presumably, precipitation played some role in removal as both metals can form carbonates/hydroxides (Albrecht 2011, Emamjomeh 2011). The breakthrough curve as seen in Figures 6, 54, and 55 display sharp sigmoidal shapes, indicating the removal mechanism of aluminum was likely dominated by available surface sites. The breakthrough curves of copper (Figures 56-58 in the appendix) show this same behavior. Both aluminum and copper removal were better in the column experiment than the batch where 76% of aluminum and 32% of copper was removed. This indicates that removal is dominated by surface site interaction. Both the breakthrough curves and the performance in the batch experiment suggest that the primary removal mechanism is either adsorption or cation-exchange (with Ca^{2+}).

4.3.2 Zeolite

The zeolite used in this study was 90-95% clinoptilolite, a commonly used ion-exchange resin, and it removed 1.08 ± 0.144, 1.63 ± 0.236, and 1.55 ± 0.0481 mg/cm^3 for iron, aluminum, and copper respectively. Similar to marble, zeolite increased the pH of the solution to 7.1. This may have resulted in the precipitation of some metal hydroxides; however, the primary mechanism of metal removal is likely cation-exchange. The negative charge of zeolite is balanced with cations (K^+, Na^+, or Ca^{2+}) that can be exchanged with the metal cations in the stormwater (Reddy 2014). Ion-exchange is a surface site dependent process, and as such the iron breakthrough curve for zeolite, shown as Figure 7, was expected to be a sigmoidal shape. This logarithmic shape can be seen in the breakthrough curves for both aluminum (Figures 77-79 in appendix) and

copper (Figures 80-82 in appendix) as well. A potential explanation could for this could be attributed to the microporous nature of zeolite (Van Tassel 1994). It's possible that these small micropores are not being utilized until the binding of metal cations has occurred at the more available surface sites. This could potentially explain the slow leveling off behavior that is seen in the breakthrough curves.

The zeolite used for this experiment was rinsed with DI water prior to use to prevent the clogging of the porous bed at the bottom of the column. Zeolite is an aluminosilicate material, and in preliminary batch experiments using unwashed zeolite there was aluminum leeching that occurred. This leaching was not observed in the column experiment, indicating that the washing may be a necessary step to ensure that a significant amount of aluminum is not discharged. Additionally, the clogging that zeolite may cause could negatively impact the hydraulic properties that are important in these bioretention systems.

4.3.3 Peat Materials (APTsorb, BioAPT)

APTsorb and BioAPT are peat materials that have been processed to be a hardened granular media with a high hydraulic conductivity. These are beneficial characteristics as raw peat tends to be difficult to wet, and often requires using a large amount of sand to maintain a suitable hydraulic conductivity. APTsorb performed better than BioAPT removing 1.12 ± 0.102, 1.69 ± 0.069, and 1.11 ± 0.073 mg/cm^3 of iron, aluminum, and copper respectively. This was expected as BioAPT was developed as a microbial carrier to help assist in agricultural plant growth, whereas APTsorb was designed specifically for water treatment. The ability of peat to remove metals from the

synthetic stormwater is consistent with previous works (Gupta 2009, Kasiuliene 2018), however the mechanism of this removal remains unsettled. The breakthrough curves for both APTsorb and BioAPT for all three metals (Figures 20-37 in appendix) suggest that the mechanism(s) at play are surface site dominated. Peat has an extensive list of functional groups that are part of the lignin, hemicellulose, cellulose, and various humic substances that it is composed of (Kasiuliene 2018). The presence of these functional groups is likely essential to the metal removal ability of peat. The presence of oxygen baring functional groups makes cation-exchange one likely mechanism. Additionally, both complexation and chemisorption between the surface and the metal have been proposed as possible mechanisms (Sharma 1993).

4.3.4 Compost

Compost performed similarly to APTsorb, removing 1.73 ± 0.380, 1.91 ± 0.367, and 1.6 ± 0.255 mg/cm^3 for iron, aluminum, and copper respectively. The negatively charged surface of compost indicates that ion-exchange or complexation are the likely mechanisms of metal removal (Lim 2015). Similar to peat, composted materials tend to have abundant organic functional groups that increase the cation exchange capacity of the media (Huang 2016). This combined with the alkaline pH of the compost may promote this metal binding as the surface potential and proton competition will be diminished (Yin 2002, Lim 2015). The argument for ion-exchange being the primary removal mechanism is strengthened by the aluminum breakthrough curve as seen in Figures 9, 46, 47. Again, the sharp sigmoidal curve indicates that the removal mechanism is dependent of surface site availability. Both the copper (Figures 46-50 in appendix) and iron (Figures

51-53 in appendix) curves display this sigmoidal shape as well. It is important to recognize, however, that these curves could look significantly different if biofilms would have had the opportunity to form. It's plausible that a decrease in effluent concentrations would be seen, as some biofilms have been shown to remove copper and other metals (Orandi 2012).

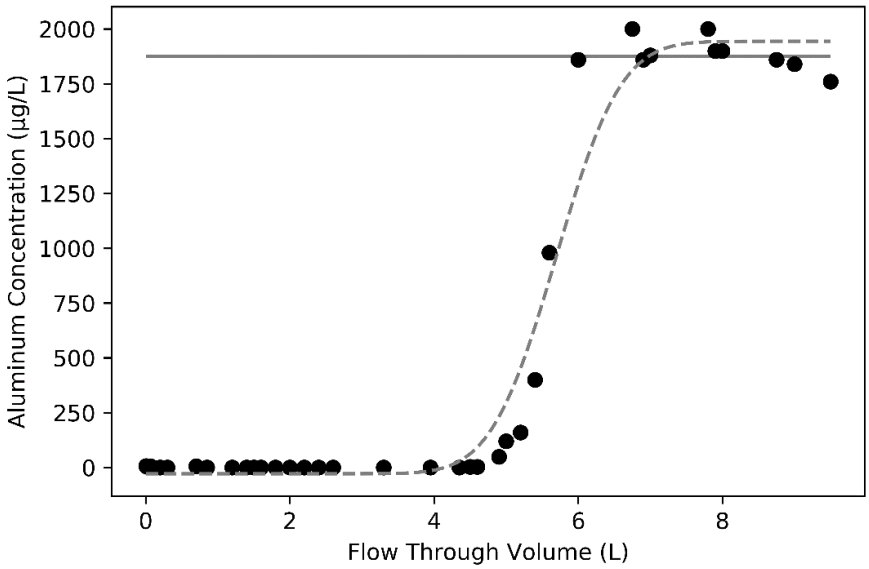

Figure 9. *Aluminum breakthrough curve for compost*

Breakthrough curve depicting the effluent concentration of aluminum after flowing through a compost column. The regression curve generated in python is represented by the dashed lines. The influent concentration of the aluminum is represented by the solid line.

4.3.5 Biochar

The biochar used for this experiment was a hardwood biochar pyrolyzed at 600°C, and removed 0.09 ± 0.051, 0.17 ± 0.023, and 0.03 ± 0.016 mg/cm^3 for iron, aluminum, and copper respectively. This was surprising given the relative success biochar had in the batch experiment removing 28% iron, 49% aluminum, and 100% copper in the batch experiment. However, it was determined that the biochar had a low

density of approximately 0.305 g/cm^3. This led to a significantly smaller volume of biochar in the columns than was present in the batch experiments.

The performance of biochar in these bioretention systems is largely dependent on the properties of the biomass used, and the pyrolysis temperature. The presence of oxygenated functional groups on the surface of biochar make cation-exchange the primary mechanism of heavy metals removal (Mohanty 2018). Cation-exchange is a surface area dependent process, and hardwood biochars have been shown to have less surface area then softwoods or other waste materials due to their relative resistance to thermal decomposition (Mukome 2013). Additionally, the high temperature at which pyrolysis occurred likely caused a sharp decrease in the oxygen-containing functional groups on the surface, which would decrease the cation exchange capacity as well (Dong 2014). The sensitivity of biochar characteristics based on these variables indicates that the results reported here are only indicative of this specific biochar. Despite the metal removal capacity being low relative to the other types of biochar the breakthrough curves for copper (Figures 10, 41,42), aluminum (Figures 38-40 in appendix), and iron (Figures 41-43 in appendix) do support an ion-exchange and/or complexation-based removal

mechanism.

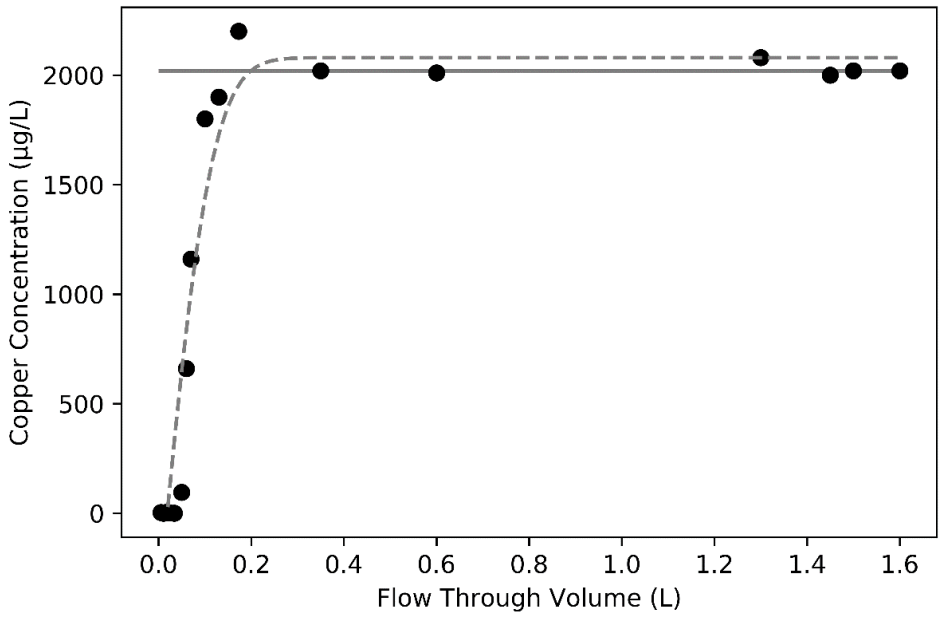

Figure 10. *Copper breakthrough curve for biochar*

Breakthrough curve depicting the effluent concentration of copper after flowing through a biochar column. The regression curve generated in python is represented by the dashed lines. The influent concentration of the aluminum is represented by the solid line.

4.3.6 Sand

Sand showed no significant removal of any of the three metals, which consistent with the previous studies (Reddy 2014). Sand was included in this study as a control as it is a commonly used material in biofilter designs due to its low cost and availability. While sand failed to remove dissolved metals, the small particle size does allow for the capture of suspended solids and particle-bound metals.

4.3.7 Vermiculite

Vermiculite was able to remove 0.845 ± 0.011 mg/cm^3 of Aluminum but showed little iron or copper removal (< 0.1 mg/cm^3). This was surprising given that vermiculite was shown to remove 53% of iron in Figure 3, and 80-100% of dissolved copper and iron in a batch reactor study by Al-Anbari et al. (2008). One possible explanation is that the vermiculite has an extremely low density of approximately 0.00172 g/cm^3. As such approximately 100 times more media was used in the batch experiment than was used in the column experiment. This could explain the lack of removal seen in the copper (Appendix Figures 71-73) and iron (Appendix Figures 74-76) breakthrough curves.

Perhaps more importantly was the vermiculite being significantly less dense than water which resulted in the column experiment resembling a fluidized bed. This effect may have caused portions of the stormwater to flow around the vermiculite and not be exposed the surface sites. The primary metal removal mechanisms of vermiculite are either cation exchange or inner sphere complexation, both of which are surface site dependent, this fluidized effect may account for the lack of removal (Stylianou 2007). Additionally, these two mechanisms in vermiculite have been shown to be at least partially dependent on the pH of the water. In a study by Malandrino et al (2006) it was shown that copper removal by vermiculite increased from 20% to 90% when the pH was increased from 5 to 7. This would explain why in batch experiments using stormwater from the site (pH=6.3) vermiculite showed removal of both iron and aluminum. Studies have used a combination of vermiculite with other media in column experiments to mitigate the fluidization issue (LeVevre 2015). In combing vermiculite with a media that

has no dissolved metal removal ability (such as sand) the removal capacity of vermiculite could be redetermined in future experiments.

4.4 Simulation of Media Treating 15 years of Stormwater Runoff

To contextualize the results presented in Figure 8, the volume of media needed to treat the runoff at the site for 15 years was estimated. To determine these values the pollutant loading of the retention pond needed to be estimated. This was done using the Stormwater Management Model (SWMM). SWMM is a dynamic rainfall-runoff simulation modeling tool developed by the EPA. This is a tool that can model how imported rainfall data will move through BMPs on site, estimating both the flow through these systems and the pollutant loading.

To provide anonymity to our industrial partner, Figure 11 shows the model of the site in SWMM with the background image removed. The *S* labels on Figure 11 denote sub-catchments, which are areas that are assumed to flow to the same outlet. The flow of runoff from these sub-catchments are denoted by the dashed lines. Sub-catchments can be a combination of surfaces, in this case asphalt and turfgrass. The percentages of each surface type were calculated using QGIS (Ver. 3.6.3) and imported into the model. The thick black line represents the swale, the *J* labels denote nodes where runoff enters the swale for the purpose of the simulation. These different *J* nodes were included to better estimate the ability of the swale to attenuate peak flows, as not all the stormwater would flow the entire length of the swale. Water in the swale flows from the entry nodes along the black line through *C4* which represents the culvert flowing underneath the road on site. *C4* empties into *Out1* which represents the retention pond. The annual pollutant

loading of the overall catchment basin is calculated at *Out1* as all the sub-catchments being displayed in Figure 11 flow to this point.

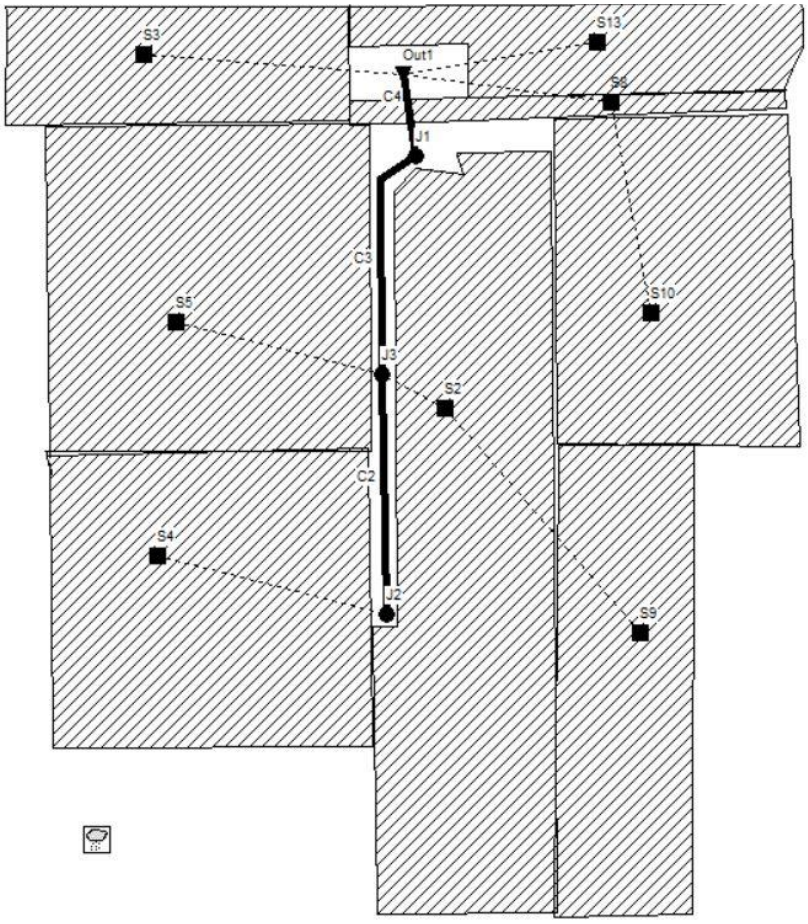

Figure 11*. The sampling site modeled in SWMM*

This figure shows the configuration of the model used to calculate the runoff of the site. The configuration was determined by overlaying a GIS image of the site (image not shown to protect the anonymity of the site). *S:* sub-catchments. *J*: Input points to swale. *Black Line*: Swale. *C4*: Culvert. *Out1*: the retention pond. *Dashed lines*: Represent flow of runoff.

Each of the units described previously are characterized individually; considering the surface roughness, depression storage, infiltration rates, and slopes. Tabulated Manning's roughness coefficients were used to determine the surface roughness values (Manning et al. 1997). The USDA soil database was used to determine that the soil on the

site is comprise of silt loam at the top three inches, silty clay loam between 3-5 inches, and clay below 5 inches. The infiltration rates used for these soils were as reported by the MPCA (MCPA 2019). The depression storage is the amount of water that is stored due to sloped depressions on the surfaces. Tholin et al. (1960) calculated the value of depression storages for various surfaces. The turfgrass and impervious surface values reported were used for this model. The slopes of each of the catchment basins were estimated by onsite measurements.

The annual pollutant loading for each simulation was calculated using the concentration of pollutants as reported in Table 5, and the Event Mean Concentration (EMC) method. The values in Table 5 are the average of the stormwater events in June and July of 2018. The EMC method assumes that the runoff from each of the sub-catchment basins has the same concentration of pollutants throughout the entirety of rain event. This is likely a false assumption for a few reasons. Firstly, as mentioned previously the sources of metal deposition likely occurs on the impervious surfaces as opposed to those covered in grass. This issue is mitigated to some degree because the collection of stormwaters occurred at the outfall of the culvert, which includes a combination of the runoff from several sub catchments. The second issue is that the concentration of pollutants in the stormwater will decrease over the course of a rain event. This is an issue as the collected stormwater (as described in Chapter 2) is from the first flush of the storm event, when the concentrations of pollutants would be the highest. As a result, the average pollutant loading of the retention pond as described in Table 6 is

likely an over estimation. To get the true EMC values of a rain event the concentration would need to be tested continuously throughout the course of the entire event.

Table 5. *Simulation Results*

SWMM was run using the EMC method, with the concentration values below as the EMCs for each of the three metals. The simulation was run 12 times using precipitation data from 1996-2008 collected from the Duluth International Airport. The average results of the annual pollutant loading are displayed below with the standard deviation.

Pollutant	Concentration (µg/L)	Average Annual Loading (kg)
Iron	140	0.603 ± 0.153
Aluminum	160	0.757 ± 0.187
Copper	6.55	0.187 ± 0.006

The simulation was run using precipitation data collected by the National Oceanic and Atmospheric Association at the Duluth International Airport. 12 simulations were run using precipitation data from 1996-2008, which was reported in 15-minute increments. While more recent data is available, data after 2008 is not downloadable in a file type currently compatible with SWMM. Table 5 shows the average pollutant loading from the 12 simulations.

To help display how efficiently biofiltration can treat stormwater runoff the required volume of each media to treat the pollutants of concern for 15 years is presented in Table 6. This estimation is based off the average annual pollutant loading of each metal as described in Table 5 for the 3.2-hectare catchment basin of the sampling site. Similar to Table 5 this is likely an overestimation of the required volume of media. As expected, the volume of marble needed to treat the runoff is significantly smaller than any material by almost a factor of 2. The current retention pond on the site has an area of

approximately 850 m^2. If we assume that the biofiltration media layer is 8 inches (0.20 m) as is the recommended minimum by the MPCA, every media except sand and vermiculite would take up a smaller footprint than the retention pond. In the case of marble, it would require only a 13.9 m^2 footprint, which would be a reduction in by nearly 98%. Granted, a filter of this size wouldn't be able to properly attenuate the peak flow of the runoff, however, this does show how effectively this technology can treat dissolved metals in stormwater. Retention ponds have shown mixed abilities at removing metals, with studies showing the removal of copper ranging from 23-61% (Harper 1988, Muthukrishan 2006). A properly implemented biofiltration basin could both attenuate the runoff and increase the quality of the discharged stormwater.

***Table 6**. Volume of Each Media Required to Treat Metal Pollutants*

Using the results in Table 5, the volume for each of the media tested to remove 15 years of pollutants was calculated and displayed.

Media	**Volume needed to treat Iron loading for 15 years (m^3)**	**Volume to treat Aluminum loading for 15 years (m^3)**	**Volume to treat Copper loading for 15 years (m^3)**
APTsorb	8.01	6.73	1.80
BioAPT	25.6	12.5	2.72
Biochar	98.4	65.5	2.72
Compost	5.22	5.94	1.23
Marble	0.841	2.79	0.972
Sand	292	778	117
Vermiculite	143	13.4	19.2
Zeolite	8.37	6.70	1.29

4.5 Conclusions

Five of the eight media tested in the column experiment provided substantial metal removal. Due to the compressed time scale of the column experiment it is likely that only mechanical and chemical removal mechanism are accounted for. In that regard, marble performed the best by a significant margin for iron and aluminum removal. The removal capacity of iron was never determined as the column didn't have any iron in the effluent after running through over 7000 bed loads of synthetic stormwater. The high content of calcium carbonate likely played a role in the removal abilities of marble. Calcium carbonate increased the pH and provided an easily exchangeable ion that could promote ion-exchange.

The removal of copper, however, was much closer between the five media. The removal of copper is of particular interest as out of the three metals being tested it is the most toxic to aquatic organisms, and as such the NPDES permitting levels are the significantly lower. For this reason, five media (APTsorb, compost, zeolite, marble, and sand) will be looked at in an additional column experiment to determine if they possess any microbial pollutant removal abilities.

5. Fecal Indicator Bacteria Removal from Synthetic Stormwater by Various Media

5.1 Introduction

Chapter 5 discusses the design and results of a column experiment to evaluate the capability of media to remove commensal and pathogenic fecal contaminants from

stormwater. *E. coli* indicator bacteria was used as a measure of microbiological water quality. The synthetic stormwater inoculated with *E. coli* was pumped through downwards flowing columns continuously for a short period of time (up to 56 hours). A bromide tracer test was also be performed before and after the 56 hours to determine what effect *E. coli* capture had on the hydraulic properties of the biofilter media.

5.2 Experimental Design

The experiments were conducted using the flow-through column system as described in section 4.2 with two modifications (Figure 12). The pre-filter column with the 0.22µm frit size as used in the Chapter 4 column experiment was removed to avoid filtering *E. coli* out of the synthetic stormwater. Prior to starting the experiment, a 5% bleach solution was run through all the tubing and columns to sterilize the system. After sterilization, DI water was run continuously through the system for 24 hours to ensure that no residual bleach remained.

A lysogeny broth (LB) solution (Thermo Fischer) was used as the medium for the *E. coli* cultivation. *E. coli* were grown in LB medium to an optical density at 600 nm (OD_{600}) of 0.7-1.0. The LB was autoclaved and allowed to cool to room temperature. 1mL of *E. coli* stock culture was added to the room temperature LB. This solution was incubated at 30°C for 24 hours after which the OD_{600} measurement was taken to ensure that cell growth had occurred. The reference used for this reading was the uninoculated LB. The *E. coli* culture was then refrigerated at 4°C until use. Before inoculating the synthetic stormwater, the culture was gently mixed at room temperature for 1 hour to slowly warm the culture and ensure that the cells were evenly disturbed within the test

tube. After the 1 hour, a spectrophotometric measurement as taken again. Equation 4 was used to approximate the coliform units/mL.

Equation 4. $E.coli\ cell\ count\ approximation$

$$\frac{\#of\ cells}{mL} = (absorbance) \cdot (8 \times 10^8 cells/mL)$$

This approximate value was used to inoculate the synthetic stormwater within the desired range (97000-290000 MPN/100mL). This concentration is based off the typical range found in industrial stormwater as reported by the Minnesota Pollution Control Agency (MPCA 2017). After adding the culture to the synthetic stormwater (1L sterile polypropylene container), it was gently mixed, and allowed to sit for 30 minutes before beginning the experiment. The stormwater solutions were covered with parafilm to minimize any potential outside contamination. A fresh stormwater solution was made every 24 hours to ensure that the concentrations of *E. coli* in the influent remained constant.

The synthetic stormwater was fed into to the column with a flow rate of 60±4 mL/hour for up to 80 hours. The *E. coli* in the effluent was enumerated at 1, 8, 24, and 56 hours. The influent concentration of *E. coli* was tested every 12 hours for the duration of the experiment. Additionally, a control column with no media present was run to ensure that no *E. coli* was being removed in the porous bed at the bottom of the columns.

To determine the effect of *E. coli* removal on the hydraulic conductivity of the media, a bromide tracer test was performed at the beginning and end of the experiment. Control columns contained each media and had non-inoculated stormwater pumped

through them. A 40mg/L bromide solution was made from dissolving potassium bromide (99.9%, Arcos Organics) in DI water, and was injected into each column in a 10mL pulse. Bromide concentrations would be determined as described in section 2.4.2.

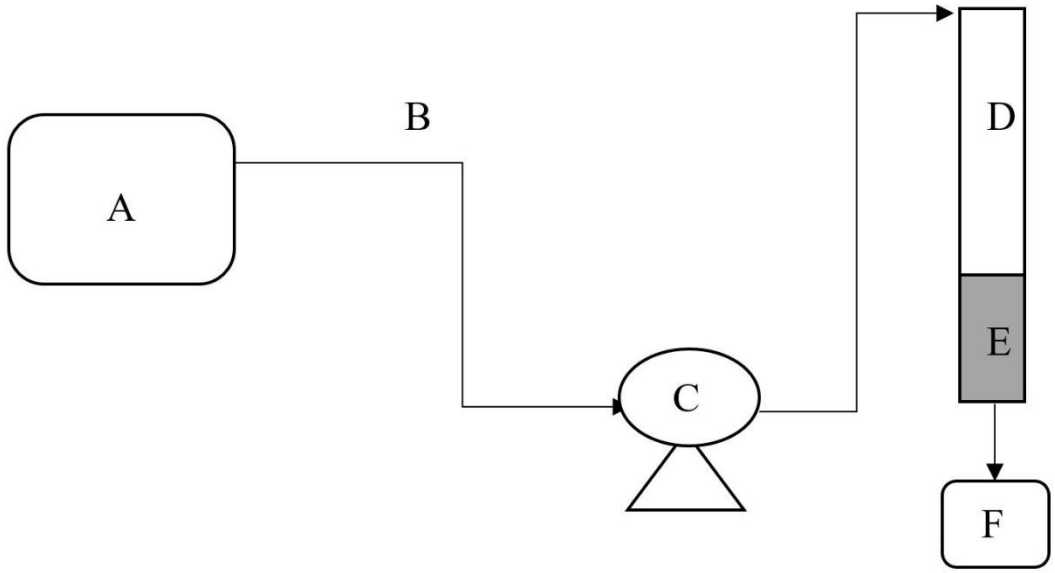

Figure 12. *FIB column experiment schematic*

A schematic of the FIB experimental setup. Unlike the Figure 4, each column has its own reservoir. A: 1L polypropylene reservoir. B: Platinum cured silicone tubing. C: Peristaltic pump. D: Glass media column. E: Media. F: Polypropylene centrifuge tube.

5.3 Fecal Indicator Bacteria Testing

The Colilert Quanti-Tray/2000 Method (EPA method 9223B) was used to determine the *E. coli* concentrations. This method uses the Most Probably Number method and has a range of 0 – 2419.5 MPN/100mL. Due to the high concentration of *E. coli* in the synthetic stormwater all samples were diluted by a factor of 1000 using DI water. Samples were prepared in 120mL sterile bottles that have been preloaded with sodium thiosulfate. The Colilert-18 reagent is added to the sample, shaken vigorously,

and allowed to dissolve. After both the reagent and thiosulfate had fully dissolved the sample was poured into the quanti-tray which is sealed using the sealing machine (IDEXX). The trays are then immediately placed into a 35°C incubator. After 24 hours the trays are examined, a yellow cell indicates the presence of a coliform bacteria, a cell that fluoresces under a UV-light indicates the presence of *E. coli*. The positive cells were counted, and the IDEXX MPN table was used to determine the MPN of cells present in the solution.

5.4 Results/Discussion

Figure 13 shows *E. coli* removal during an initial experiment over 5 hours. All of the media were capable of removing over 50% of *E. coli* initially except for compost. Both sand and marble are able to remove the *E. coli* well, with sand removing over 75% for the duration, and marble removing 100%. The removal of APTsorb is lower than sand and marble, however values above 40% are seen over the 5 hours and could potentially be showing a removal rate that trends upwards over time. The successful removal of *E. coli* by these three media meant they would be examined in the longer scale experiment.

Figure 13 shows that the *E. coli* in the effluent from the compost column increased as the experiment progressed, suggesting that compost may have leached *E. coli*. Because leaching was seen immediately at the one-hour mark (~12 bed loads) it is likely that some *E. coli* was present in the compost prior to running the column experiment. This is feasible, as composed materials go through a thermophilic stage during production, where temperatures reach 55-65°C, however, *E. coli* can survive in temperatures of up to 70°C. The trend of increased *E. coli* leaching over time in Figure 13

suggests that it's also possible that the nutrient rich compost promoted growth of *E. coli* in the media over the course of the experiment.

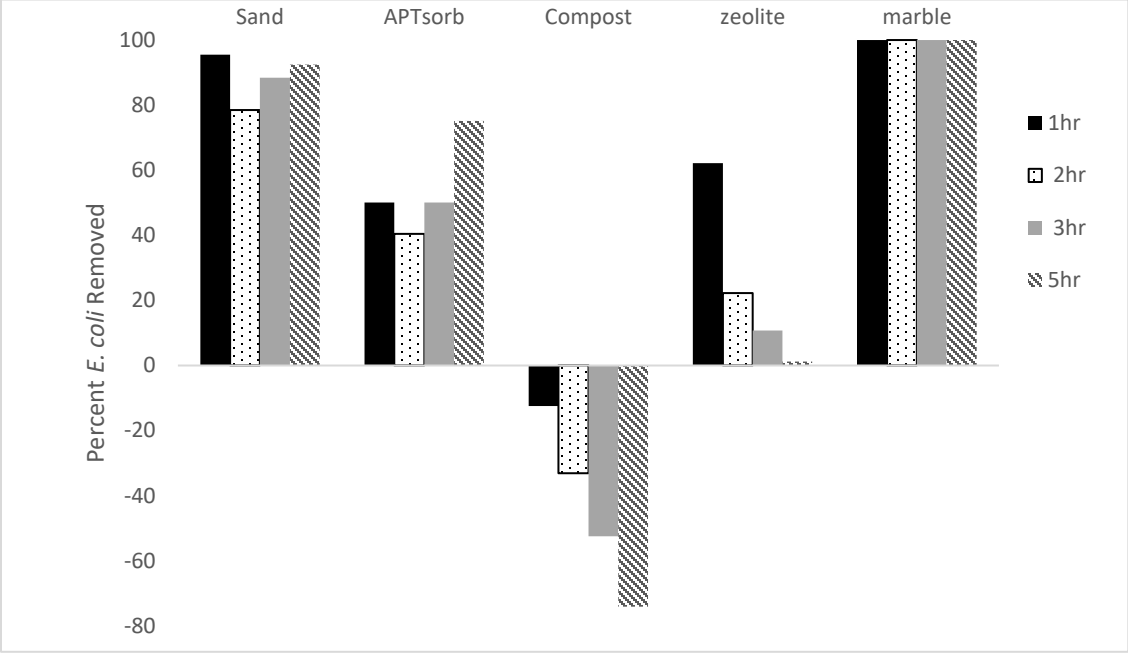

Figure 13. *FIB screening experimental results*

The percentage of FIB *E. coli* removed from the synthetic stormwater at a given time interval during the 5 hour experiment.

Zeolite was able to remove over 60% of the *E. coli* at the 1-hour (~11 bed loads) mark, however decreased steadily until removing only 2% at the end of the experiment. Although the surface area of zeolite is likely much greater than any of the other materials due to its microporous structure, the negative surface charge limits its capacity for adsorbing *E. coli* (Widiastuti 2008). Several studies have modified the surface charge of zeolite by treating it with long-chain cationic surfactants such as hexadecyltrimethylammonium chloride (HDTMA) (Bowman 2003, Schulze-Makuch 2002). HDTMA possesses a permanent positive charge and undergoes cation exchange

with the inorganic cations on the surface of the zeolite (Widiastuti 2008). Zeolites treated with HDTMA achieved 100% removal of *E. coli* (Bowman 2003). Natural zeolite has been used effectively in wastewater treatment; however, removal depends of the formation of a bacteria layer, which can take weeks to form (Princz 2005). Based on these results, sand, marble, and ATPsorb were examined for the removal of *E. coli* over 56 hours.

Figure 14 displays the results from the 56-hour experiment and shows that both sand and marble performed well removing over 90% of *E.* coli. The sand column was able to consistently remove between 90-100% of the *E. coli* over the course of the experiment. This removal rate is consistent with the literature that which indicates that slow sand filters typically remove between 83-100% of *E. coli* (Yogafanny 2014, Klenheinz 2008). Removal rates in these slow sand filters have been seen to increase over time, removing 98-99% as the formation of a schmutzdecke on the surface of the filter occurs (Unger 2008). Schmutzdeckes are a form of biofilm in that they are biologically active, and can consist of bacteria, algae, protists, and macroinvertebrate (McNair 1987). Due to the short timescale of these experiment the removal mechanism was likely limited to adsorption and/or mechanical filtration and was thus dependent on the particle size, and depth of the media (Stevik 2002).

Similar to sand, marble was successful in removing the *E. coli,* consistently removing 100% throughout the duration of the experiment. Figures 15 and 16 show the results of the bromide tracer tests from which the HRT was calculated for sand and marble respectively. The HRT of sand increased from 11 minutes to 19, and the marble

increased from 10 minutes to 18. This increased HRT suggest that the *E. coli* are likely being removed via straining or adsorption and clogging the pore space in the media. This clogging was attributed to the *E. coli* as no difference was observed in the HRT for the columns that were run with the synthetic stormwater that was not inoculated (Figures 85-87 in appendix).

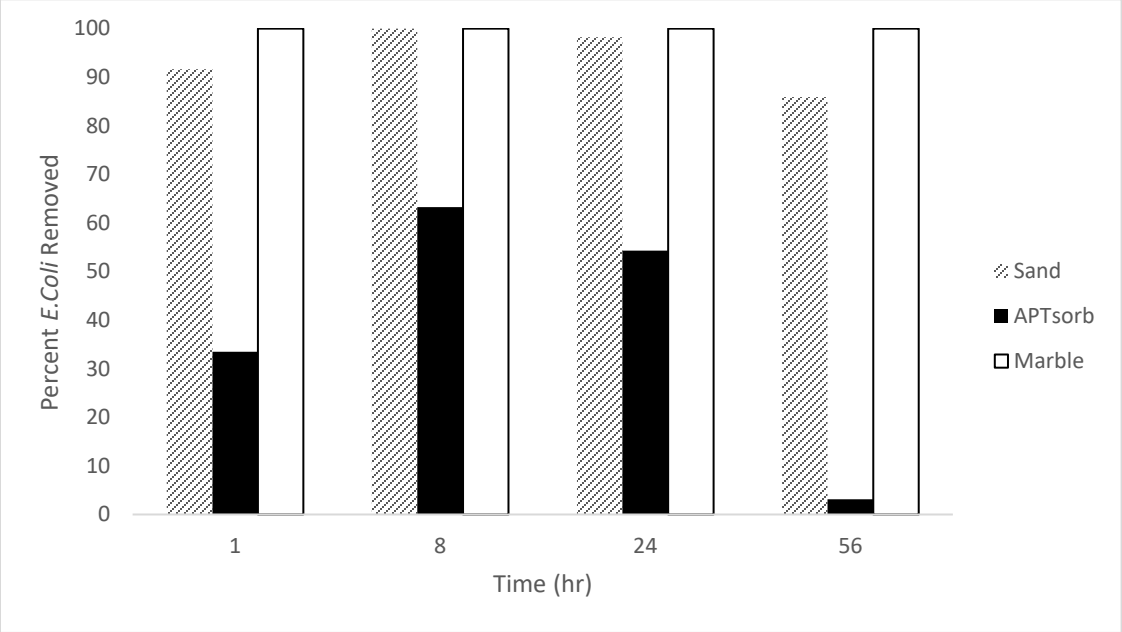

Figure 14. *FIB column results*

Percentage of *E. coli* removed by 5.3cm^3 of each media at the given time intervals during a continuous flow column experiment.

No literature was found on the ability of marble to remove *E. coli*, however, similar to sand it is assumed that the removal mechanism is not biologically based. This would indicate that the removal ability would likely be dependent on particle size, and column depth. As such the similar removal ability to sand should be expected. One explanation for the difference in removal rate could be the surface roughness of the media. It's possible that the sand had a smoother surface than the marble, which was

crushed down to size using a pulverizer. Irregularities in the grain surface roughness have been shown to increase sticking efficiency (Matthess 1991).

Another potential explanation in the difference in effectivity between the sand and marble could be the differences in surface charge. *E. coli* has a negatively charged surface, and as such positively charged media could enhance the likelihood of adsorption (Foppen 2004). Calcite tends to have a point of zero charge (pH_{pzc}) of between 9.5-10.9mV (Somasundaran 1967) whereas silica sand has a pH_{pzc} of approximately 7.2 (Foppen 2004). Both of these values are higher than the pH of the synthetic stormwater (pH~5), and as such both have a weak positive charge. Because the pH_{pzc} of the calcite is higher than that of the sand, it would be feasible that a potential increase in adsorption efficiency of the media could explain the difference in removal rates.

Additionally, it seems plausible that given more time a schmutzdecke may form on the surface of the marble filter as well, which could promote continued *E. coli* capture over a long period of time. This is an area that should be explored more, as the changes in the water chemistry caused by the calcium carbonate in the marble could hinder or promote this growth.

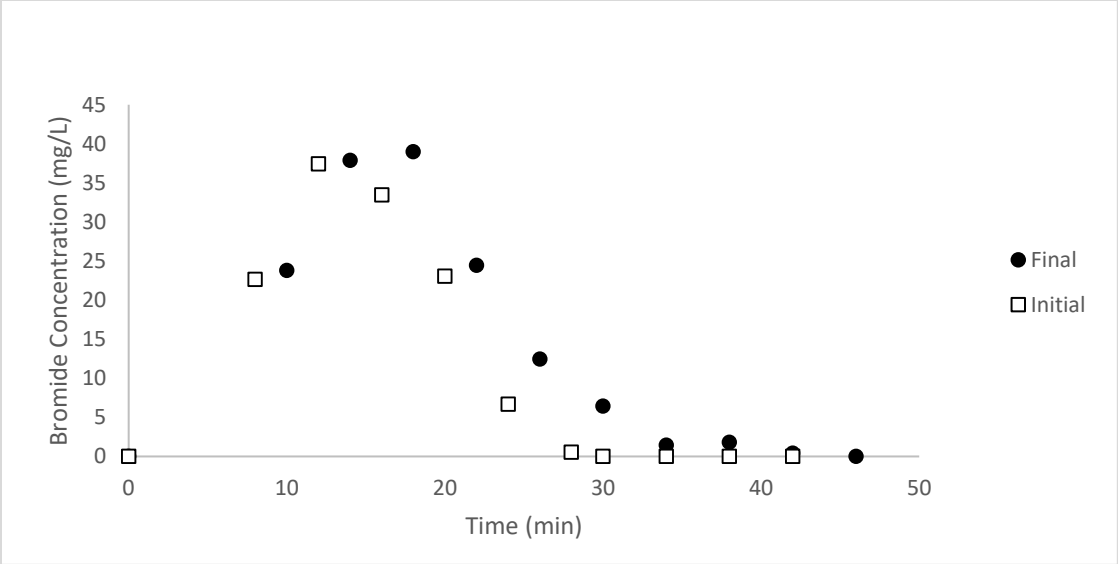

Figure 15. *Sand column bromide tracer test*

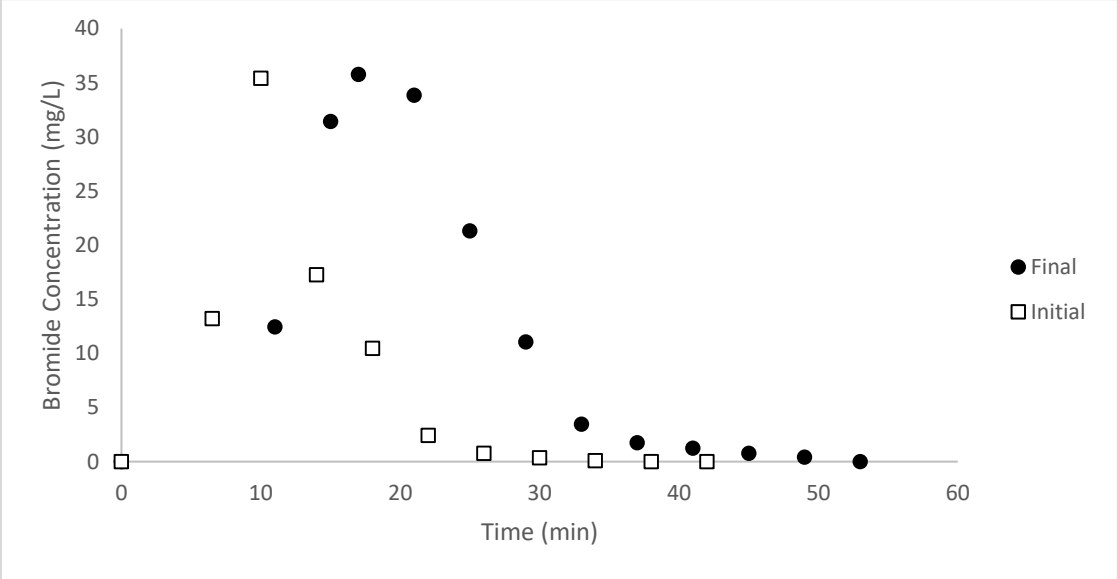

Figure 16. *Marble column bromide tracer test results*

APTsorb also saw an increase in HRT, however a much smaller increase from 17 to 19 minutes (Figure 17). This material showed 30-60% *E. coli* removal for the first 24 hours but dropped to 3% after 56 hours (Figure 14). These results indicate that the removal ability of APTsorb in terms in mechanical filtration is small relative to sand and

marble. The pH_{pzc} of peat moss has been reported as approximately 3.42 (Bakatula 2018). Although this peat material has been processed, it would likely retain a similar point of zero charge. Because the point of zero charge of peat is lower than that of the synthetic stormwater, this material would have a weak negative charge. This would likely adversely affect adsorption ability of the material. However, as mentioned previously organic materials such as APTsorb enhance biofilm formation, so if the columns were allowed to run for a longer period of time it is possible that the removal rate would increase.

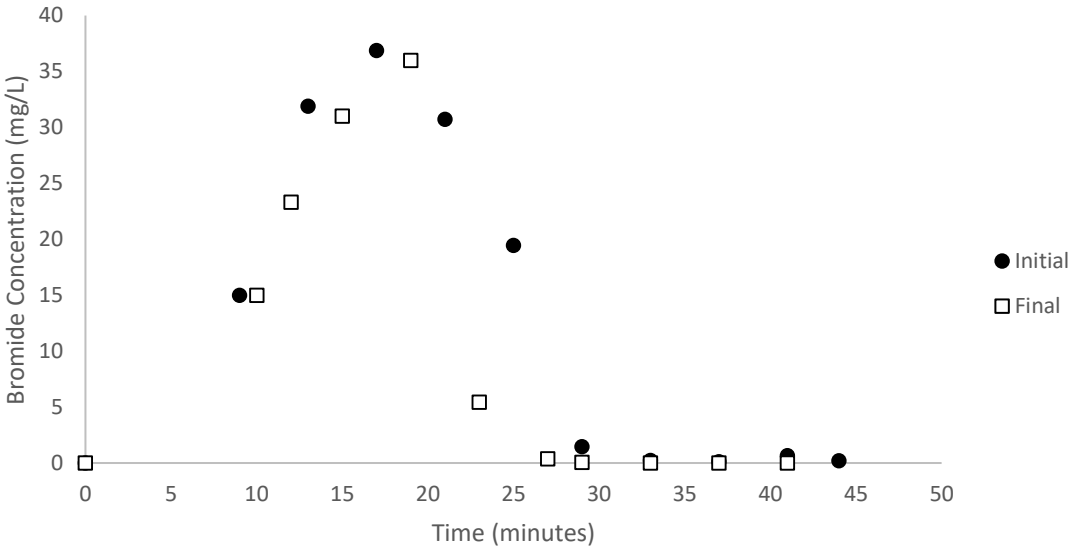

Figure 17. *APTsorb column bromide tracer test results*

5.6 Conclusion

In the short-term (5 hours) experiment, it was determined that compost leached *E. coli*¸ and the capacity of *E. coli* removal by zeolite was marginal. Of the media tested in

the 56-hour experiment, APTsorb showed promise in the beginning removing between 30-60%, however by the end of the 56 hours was only removing 3% of the *E. coli*. Marble performed the best removing 100% of *E. coli* over the duration of the experiment. Sand also performed well by consistently removing between 90-100%. Similarly, to the metal capacity experiment it is likely that the only mechanisms being accounted for in this experiment are the mechanical mechanism. Biological removal by schmutzdecke formation has been well documented in the slow sand filters and could be expected to either increase or maintain the levels of removal reported in this study.

6. Overall Conclusions on the Metal and FIB Removal from Industrial Stormwater using Various Media

Biofiltration has become one of the most commonly employed best management practices in dealing with stormwater in the United States (Davis 2009). Biofiltration is typically employed in urban, agricultural, or commercial settings as opposed to an industrial one. While stormwater itself is inherently variable, the pollutants present in the stormwater depend greatly on the land use of the catchment area. Different media used in the filtration systems exhibit differing effectivity in removing metals, anions, bacteria, *etc*. As such these bioretention cells are not ubiquitous and need to be tailored to treat the pollutants of concern for each site.

This study determined the pollutants present in the stormwater runoff from an industrial site, and quantified the ability of eight media (APTsorb, bioAPT, biochar,

compost marble, sand, vermiculite, and zeolite) to treat the dissolved pollutants of concern (Al, Cu, Fe, and bacteria). Due to the relatively short length of the column experiments the removal mechanisms accounted for in this study include those of the mechanical and chemical nature. Adsorption and ion-exchange are the two mechanisms that were likely the most prevalent in the media tested.

Removal of dissolved metal was achieved in all the media with the exception of sand. Of the media tested, marble performed the best, removing over 10 mg/cm^3 of iron, 4 mg/cm^3 of aluminum, and 2 mg/cm^3 of copper. The increase in pH, caused by the marble likely accounted for the majority of the iron removal, as iron precipitate was visible on the surface of the columns. For Aluminum and copper removal, the breakthrough curves suggest that a surface site dominated mechanism is occurring. This mechanism is likely primarily adsorption, with a small amount of ion-exchange occurring with the calcium ions on the surface of the marble.

The secondary pollutant of concern was the presence of FIB in the runoff. The ability of three materials (APTsorb, marble, and sand) were evaluated in their ability to remove *E. coli* from the stormwater. Marble again performed the best removing 100% of *E. coli* after 56 hours of continuous flow (362 bed loads). Sand also performed well in this portion of the experiment, removing 90-100% of *E. coli* throughout the duration. The removal mechanisms for both sand and marble are physical mechanisms (adsorption, straining), as 56 hours is likely not a sufficient amount of time for schmutzdecke growth. However, the growth of this schmutzdecke has been shown to reliably increase the

removal rates of sand filters, and as such the overall removal rates of all materials may increase given a longer time scale.

While marble performed the best in removing all the pollutants of concern, it was also the second most expensive material tested (behind zeolite). The objective of this study was to determine the removal capacities of each of these media in hopes that this information could be useful in future designs of biofiltration systems. While an economic analysis was viewed as outside the scope of this project, it is important to recognize that cost is a major factor in the design of these systems. Despite the high cost, the marble has shown to be very capable of removing metal and FIB, and as such could be used sparingly in filter designs. For example, adding small volume of marble to a sand biofilter system could be sufficient to adequately treat the metal polluted stormwater while only marginally increasing the cost of materials.

7. Recommendation

Based on the results from this study, a biofiltration system is recommended as a viable stormwater treatment option for the industrial site. A media layer comprised of a mixture of sand and either APTsorb or marble is recommended to capture metals (both particulate and dissolved) and FIBs from stormwater. Both the APTsorb and marble were shown to need small volumes to treat the stormwater for 15 years (Table 6) and didn't with limited leaching concerns (Figure 4). While sand performed poorly in removing dissolved metals from the stormwater (Chapter 4), the dissolved metal removal can be handled by the small volume of marble or APTsorb. However, sand has been shown to

remove particulates from stormwater (Davis 2005), and *E. coli* (Chapter 5). And although a formal economic analysis is viewed as outside the scope of this project, sand is an inexpensive material, and widely available, both which make it an attractive option. Finally, sand has a very high infiltration rate which is a desirable characteristic of media in these biofiltration systems.

A biofilter was designed for the site (Figures 18,19), using the design parameters dictated by the Minnesota Stormwater Manual (MPCA 2019). Because the design characteristics required by the MPCA are in imperial units, the calculations/results in this chapter will also be in imperial units. The MPCA recommends that biofiltration basins be used for treating stormwater from contribution areas of 5 acres or less and requires the maximum wet storage be 1.5 feet or less. The catchment basin for the retention pond is approximately 7.8 acres. The primary reason for this 5-acre recommendation is to ensure that the drawdown time of the basin is under 48 hours. The desired mechanism of draining is through infiltration through the soil at the bottom of the biofilter. This allows for additional filtration as the water percolates thorough the soil and can help assist in groundwater recharge. However, because the infiltration rate of the lower two layers of soil (clay loam, and clay) are poor it is recommended that an underdrain be installed. These underdrains are often made of PVC and should be no smaller than four inches in diameter. One underdrain should be installed for each 1000 ft^2 of basin surface area. By installing the appropriate number of underdrains and using sand as the primary component (very high infiltration rate), the concerns of the larger catchment basin can be mitigated.

The first step in designing the system was to determine the volume of water that is required to be treated. The MPCA dictates that the first inch of all stormwater flowing over impervious surfaces is the amount of water that must be treated by a biofiltration basin (MPCA 2019). This volume is referred to as the water quality volume (WQV). *WQV* is calculated using the Equation 5, where A_{site} is the total area of the catchment basin, *%impervious* is the percentage of impervious surfaces in that catchment basin, and 3630 is the conversation factor to cubic feet.

Equation 5. *Water Quality Volume*

$$WQV = A_{site} \times \%impervious \times 3630$$

The WQV of the study site was calculated to be 9905 ft^3. The biofiltration basin must be designed to attenuate the entirety of this WQV. This is done to ensure that the first flush of stormwater is fully captured and treated by the biofiltration cell. If space permits a larger volume can allow for a greater volume of water to be treated. However, it must be ensured that this storage volume can drain in 48 hours.

The current retention pond is an oval shape with diameters of 160 ft and 66 ft. Operating under the assumption that the biofiltration basin would replace the current retention pond, a biofiltration basin was designed. Figures 18 and 19 are the cross-sectional diagrams of the biofilter design (not to scale). Making use of the current retention pond is desirable as the catchment basin has been developed to route the stormwater to this area. Additionally, the swale used in routing the water helps with pretreatment in removing suspended solids and debris before it enters to the biofilter

basin. There is a storm sewer drain (*F*) directly next to the pond that acts as an overflow mechanism. This can be worked into the biofiltration design, to serve the same purpose. The maximum height allowed for ponding is 1.5ft, as such the entrance to the storm sewer will be set at 1.5ft. The height at all other points of the basin will be 1.7ft. This height differential should promote excess volume to flow through the overflow mechanism and not lead to backing up of the culvert or flooding to occur outside the basin. To prevent erosion, a layer of rip rap should be applied to both inlet from the culvert and the outlet to the storm sewer.

To determine if using the same footprint as the existing pond is an acceptable solution, it must be confirmed that the proposed design can attenuate the WQV. The wet storage volume (*V)* was calculated by Equation 6. Where the first term represents the volume of the oval not including the sloped portion, where R_1 and R_2 are the radii of the filter area, and 1.5 is the depth of the wet storage. The second term is the volume of the sloped portion, where 3.375 is the area of the triangle formed by the slope multiplied by the circumference of the pond. R_{1T} and R_{2T} represent the radii of the entire ponding area (160, 66ft).

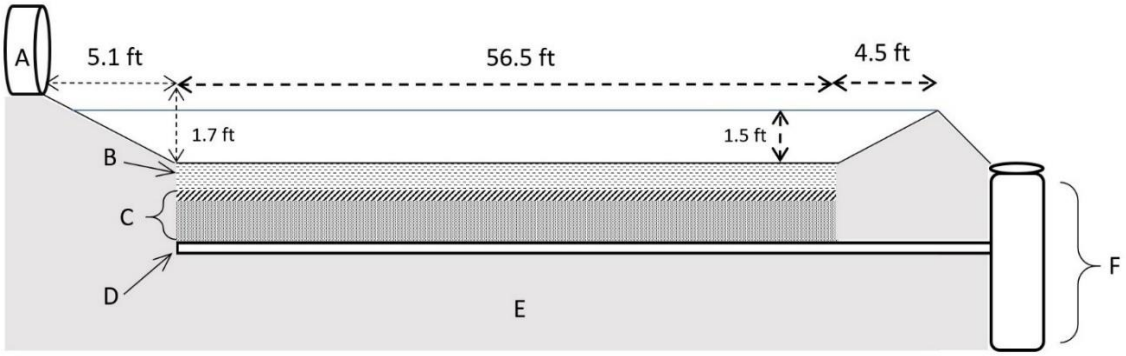

Figure 18. *Cross Sectional View of Biofiltration Design (1)*

A cross sectional view of the biofiltration basin design across the minor axis, A: the culvert where a large portion of the runoff is deposited. B: a thin layer (~3") of topsoil (promotes vegetation growth), C: 8" Biofilter layer (composition listed in table 7), D: perforated PVC underdrain (minimum diameter of 4"), E: Soil (silty loam or clay loam), F: storm sewer drain. 1.5 ft is the maximum allowed ponding area. Maximum slope height is 3:1. Figure is not to scale

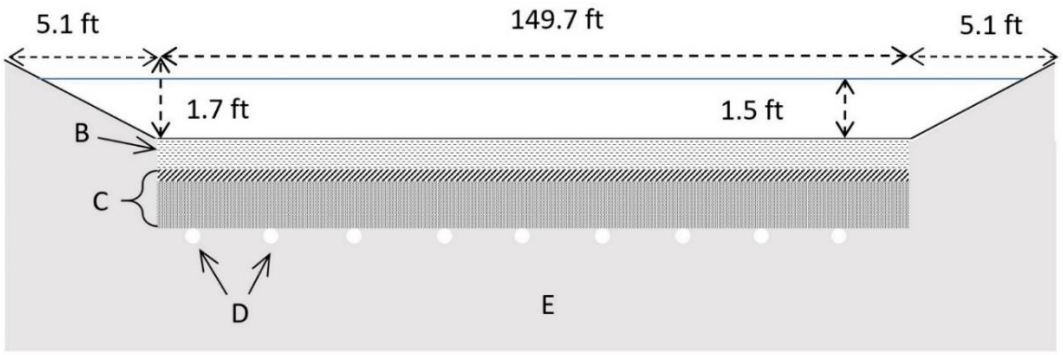

Figure 19. Cross Sectional View of Biofiltration Design (2)

A cross sectional view of the biofiltration basin design. B: a thin layer (~3") of topsoil (promotes vegetation growth), C: 8" Biofilter layer (composition listed in table 7), D: perforated PVC underdrains (minimum diameter of 4"), E: Soil (silty loam or clay loam), 1.5 ft is the maximum allowed ponding area. Maximum slope height is 3:1. Figure is not to scale

Equation 6. *Wet Storage Volume*

$$Volume = (R_1 \times R_2 \times \pi \times 1.5) + (3.375 \times 2\pi \times \sqrt{\frac{({R_{1T}}^2 + {R_{2T}}^2)}{2}})$$

In combining these two volumes, it was determined that the dimensions of the ponding area can hold 11500 ft^3 of water, which is larger than the WQV. The final aspect that must be considered in the design is the drawdown time. As mentioned previously the drawdown time must be less than 48 hours. Using the equations Equation 7 provided by the MPCA, the drawdown time (hours) can be estimated. *Depth* represents the overall depth of the media (11 inches). *I* represents the infiltration rate (inches/hour). *I* was determined by looking up reported infiltration values of sand and loamy soil (topsoil) (MPCA 2019). A weighted average based on the depth of each media layer was calculated using these infiltration rates. It was assumed that the small percentage of marble or APTsorb used in the sand layer would not significantly alter the infiltration characteristics.

Equation 7. *Drawdown Time*

$$Drawdown\ Time = \frac{Depth}{I}$$

From Equation 7 it was calculated that the system should drain in approximately 13.4 hours, well under the 48-hour limit. However, the values used are reported values, and as such can only be considered an estimate. It would be important to perform field tests to ensure that this combination of media can drain the basin sufficiently fast.

Figures 18 and 19 show three layers in the biofiltration design. The top layer (*B*) would be a thin layer of topsoil to help promote the growth of vegetation. Vegetation in these systems has shown minimal metal removal abilities, however, some plants have shown the ability to provide nutrient removal (Read 2007), FIB removal (Li 2016), and adds aesthetic value. The second layer (*C*) is the biofiltration layer, the composition of which can be seen in Table 7, will be where the majority of the pollutant removal occurs. These percentages are based off of the total amount of media required to treat 15 years of storm water (Table 6). The minimum depth of media used in these systems is 8 inches, and the rest of the volume will be comprised of sand.

Table 7. *Biofiltration Media Composition*

The percentage of each material in the biofiltration media layer of the design. Percentages based on the estimations in Table 6.

Design	Sand	BioAPT	Marble
1	93.7%	6.3%	0%
2	97.8%	0%	2.2%

The above design was included in this work to show that a biofiltration basin could replace the current BMP on site. This BMP would use the same footprint as a retention pond and increase the quality of discharged stormwater. It also shows that a relatively small addition of media can make an impactful difference on the treatment of stormwater.

8. Future Research Directions

8.1 Testing Additional Media

The nature of biofiltration means that there is always the opportunity to explore additional media, and how they interact with stormwater pollutants. As Chapter 6 explained, marble performed the best in removing all pollutants. Calcite, a major component of marble, has been shown to remove metals (cadmium, copper) and phosphorus from stormwater (Reddy 2014) due in part to forming carbonate metal precipitates. This was also seen in Chapter 4, with the deposition of the reddish-orange iron-carbonate on the marble. These studies may suggest that calcium carbonate is the primary component of the marble that promoted metal removal. Exploring different calcium carbonate bearing minerals (calcite, aragonite, vaterite) or rocks (limestone or travertine) could potentially provide a cheaper alternative that offer similar removal rates as marble.

8.2 Column Experiments using Collected Stormwater

Outside of testing alternative materials, there are experimental changes that could provide data more similar to what would be expected in a biofiltration system employed in the field. It is important to recognize that the metal capacity experiment ran in this study was done using a synthetic stormwater. This synthetic stormwater was created to resemble the water collected on site, however, does not replicate it fully. The water chemistry of runoff is complex as it picks up pollutants and forms a unique combination of metals, suspended solids, bacteria, hydrocarbons, and many other constituents. It is plausible that these additional constituents not accounted for in the synthetic stormwater

could compete for active sites on the media with the pollutants of concern for this study. Additionally, some of the removal mechanisms used by the media, such as chemical precipitation and ion-exchange, have shown to vary in effectiveness at different pH values (Berber-Mendoza 2006, Malandrino 2006).

Using collected stormwater would also provide valuable insight on how the hydraulic conductivities would change over time. As shown in the bromide tracer tests (Figures 80-82 in appendix) there was no change in the hydraulic retention time after flowing through non-inoculated synthetic stormwater. This is good, indicating that the metals being captured are not significantly altering the hydraulic properties of the media. However, as shown in Chapter 5, when the biofiltration media starts to capture the *E. coli* the hydraulic retention time increases. The stormwater collected at the sampling site often had leaves, sticks, and other debris flowing into the retention pond. This debris combined with the suspended solids, and bacteria in the stormwater could to lead clogging of the system. As discussed in Chapter 7, the drawdown time of these biofiltration units must occur in under 48 hours. Seeing how the hydraulic conductivity changes over time would be important in determining the efficacy of these media.

A column experiment could be conducted similar to the one performed in Chapter 5 with a few key differences. Instead of using synthetic stormwater the column should be run with collected stormwater. The collected stormwater could be spiked with the proper iron, aluminum, and copper salts to allow for breakthrough to be observed in a timely manner. Additionally, a bromide tracer test (as described in Chapter 5) should be run

periodically throughout the column experiment. The tracer test will provide insight on how the hydraulic retention time is changing over the course of the experiment.

One area that would need to be explored further before performing this experiment is determining how the collected stormwater may change over the course running the column experiment. In the case of most of the media tested in Chapter 4, breakthrough wasn't observed until the columns were run continuously for 3 weeks. It's possible that metals may precipitate out of solution, or the microbial contaminants present in the water will grow or die over time. One possible solution would be to continuously monitor the influent concentration over the course of the experiment. This method would be relatively time and resource intensive. A second solution would be to run the column experiments for a set period of time with each batch of stormwater collected. After this period of time, the column could be stopped until additional collection occurs. This method would introduce wetting/drying of the media, a variable that would need to be accounted for.

8.3 Modeling the Breakthrough Curves

A final area of future work could be developing a model for the breakthrough curves for each of the media. In this study an error function was fit to the breakthrough data, however this was done purely for the sake of fitting a regression curve to the data. The parameters that were optimized likely have little or no physical meaning. For the purpose of this paper, this method fit our needs. However, fitting an advection-dispersion model to each of the materials could provide insight into the mechanisms at play and the physical characteristics that effect those mechanisms. Equation 8 shows the advection-

dispersion model. This equation has three separate terms each with a model parameter (*k*, *D, v)*.

Equation 8. $Advection - Dispersion\ Model$

$$\frac{\partial c_a}{\partial t} = D\frac{\partial^2 c_a}{\partial x^2} - v\frac{\partial c_a}{\partial x} - kc_a$$

The first term represents advective transport, with the *v* term representing interstitial velocity, C_a representing concentration of the pollutant *a*, *t* representing time, and *x* representing distance. The second term is the effective diffusion coefficient, where the *D* term represents the effective diffusion coefficient. The final term is the change in concentration due to reactions, where *k* is the deposition rate constant. This *k* value will account for all the removal mechanisms of a particular media.

This transport model assumes that pollutant deposition follows first-order kinetics and is irreversible. Both of these assumptions are reasonable when the pollutant concentrations are sufficiently low, as they would be in the case of the stormwater (Grolimund 1998). In order to fit the model, the three parameters must be determined simultaneously from the breakthrough curves (Ataie-Ashtiani 1996). The numerical solution to Equation 8, is displayed as Equation 9 where M_a indicates the total mass of pollutant *a* injected into the system (Grolimund 1998). Equation 9 can be fit to the observed breakthrough data by minimizing the RMSE values. In doing this the model parameters can be determined.

Equation 9. *Solution to Advection-Dispersion Equation*

$$c(x,t) = M_a e^{-kt}\frac{x}{2\sqrt{\pi t^3 D}}e^{\frac{-(x-vt)^2}{4Dt}}$$

The efficacy of this model could be increased further by running additional columns under slightly different conditions, in a method similar to that described in Avellaneda et al (2010). In which a similar advection-dispersion model was fit to the effluent of a biofiltration system for 17 rain events. The parameters were optimized for each event and median values for each parameter was used in the validating the model. Undergoing a similar process for each of the media tested could help strengthen the model.

Overall, this modeling process could give some insight on how the transport of pollutants varies between the each of the media. Additionally, each of the pollutants will have a different model for each media, which would also provide some information on how each pollutant is transported through the media. Looking at trends across the different media could provide some insight on either the kinetics of each media (*k)* or help determine favorable physical characteristic that help promote pollutant removal.

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Appendix

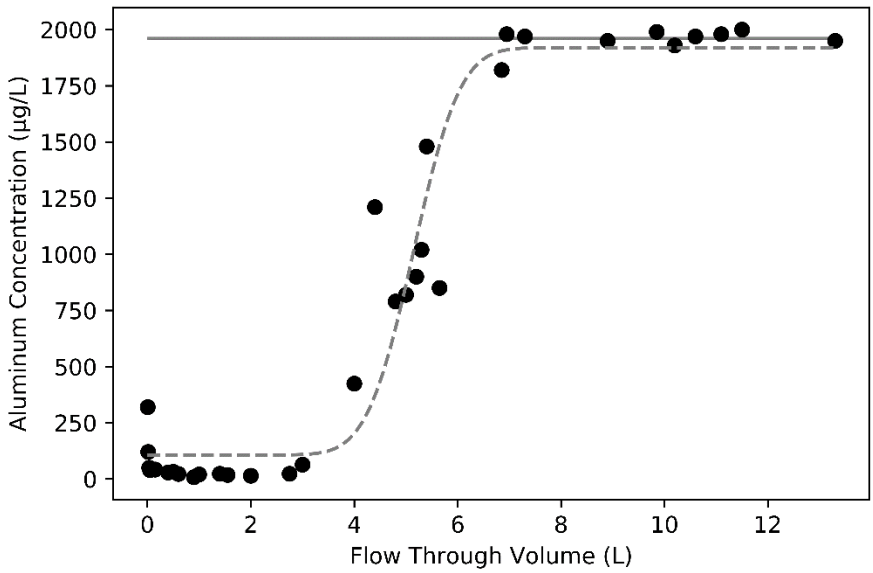


Figure 20. *Aluminum breakthrough APTsorb column (1)*

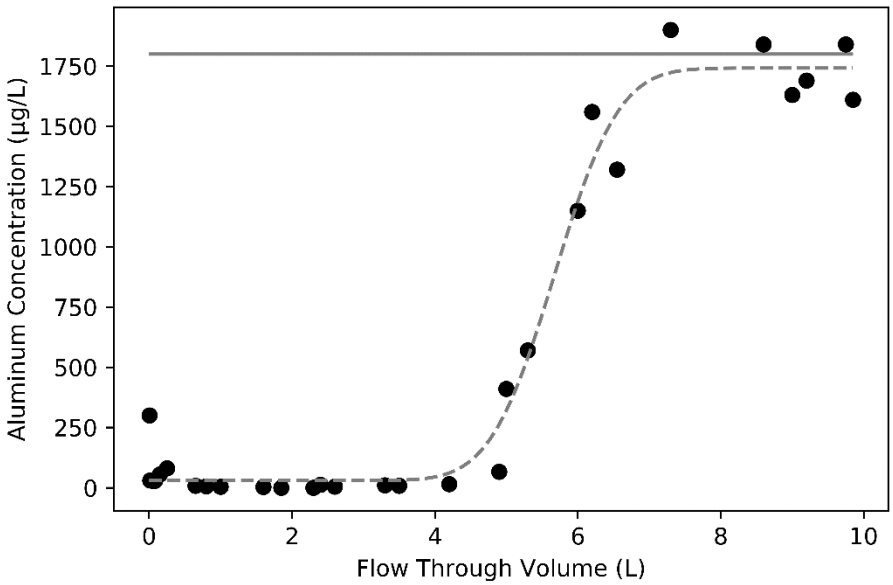


Figure 21. *Aluminum breakthrough APTsorb column (2)*

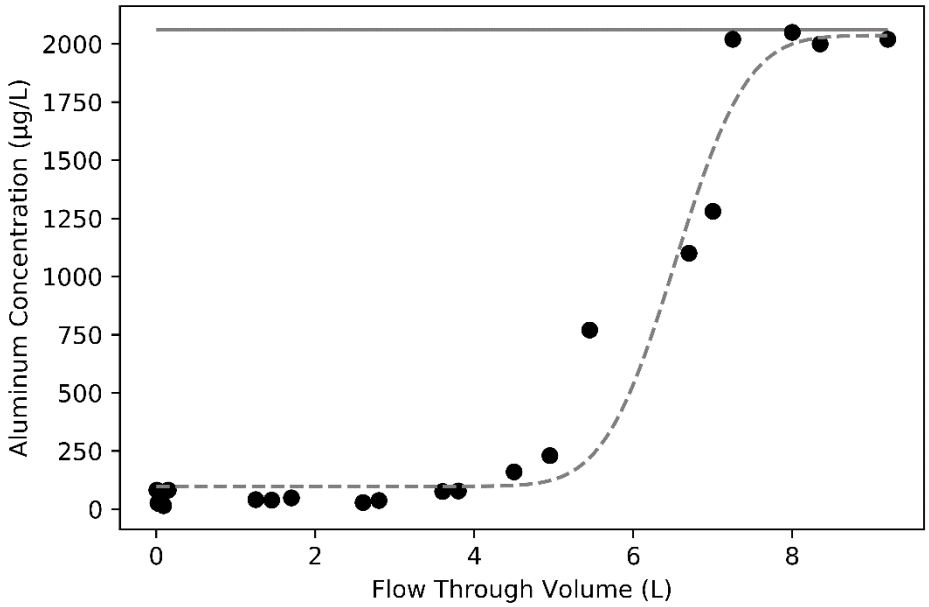
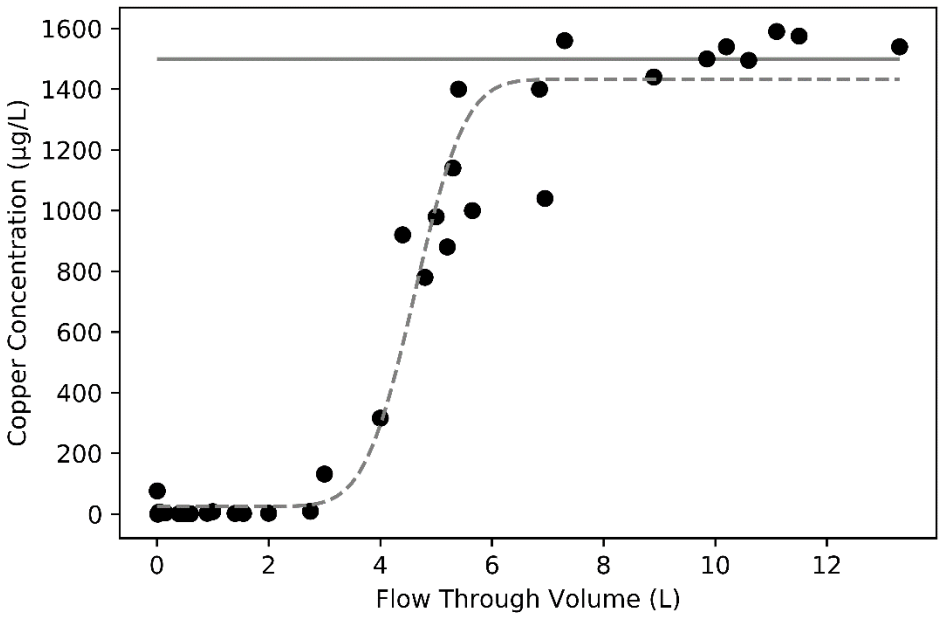


Figure 22. *Aluminum breakthrough APTsorb column (3)*



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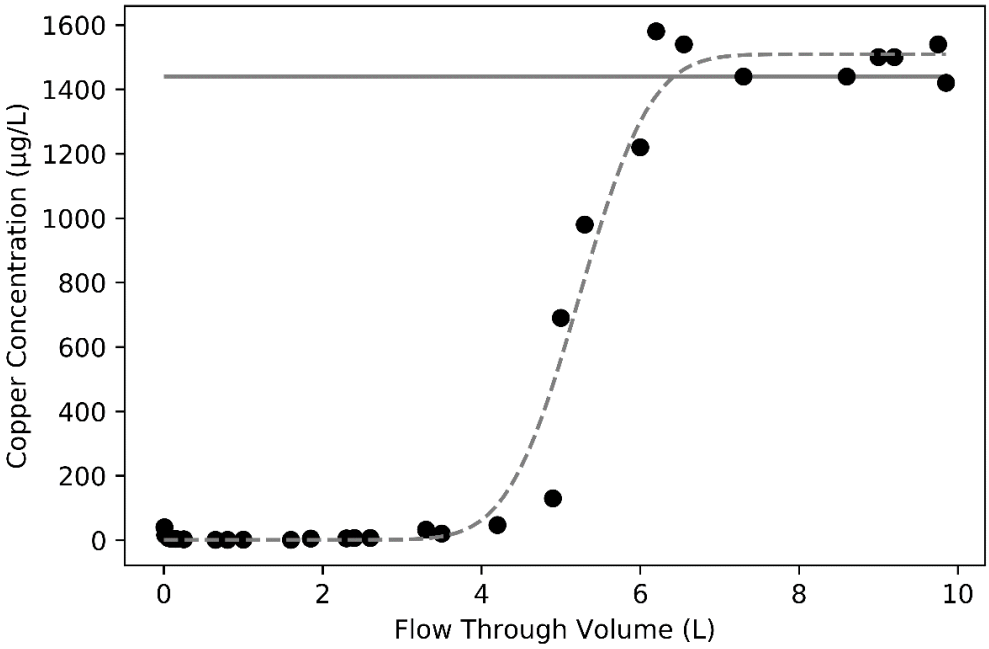

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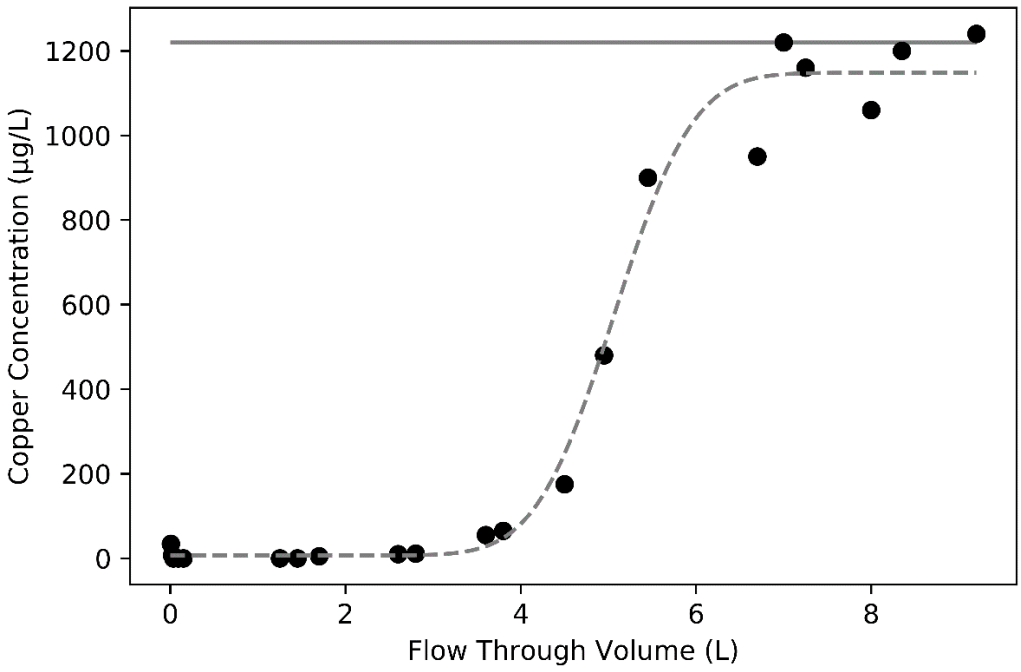

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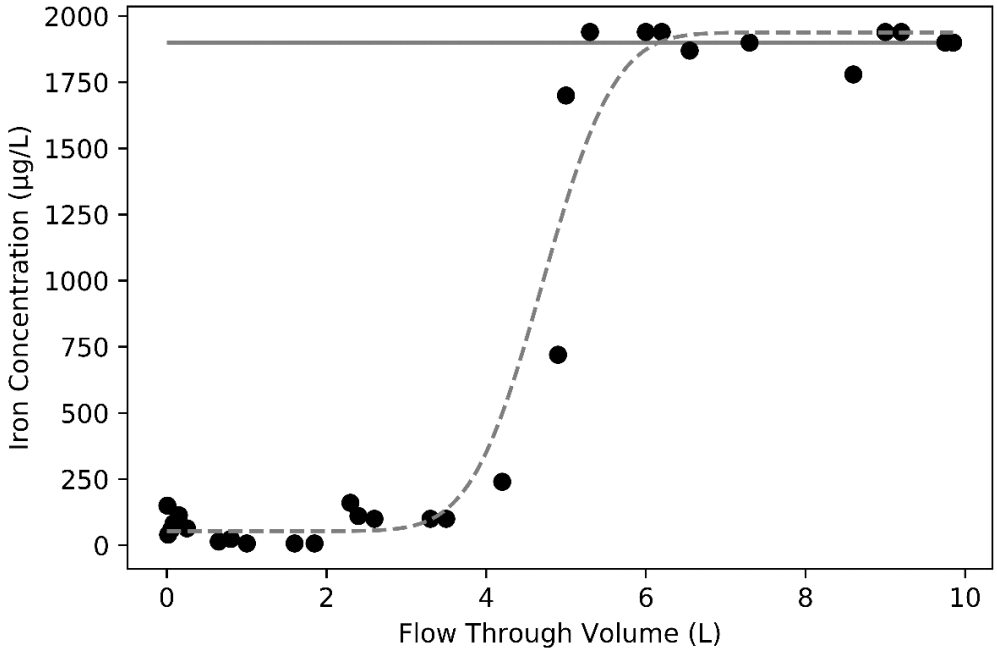

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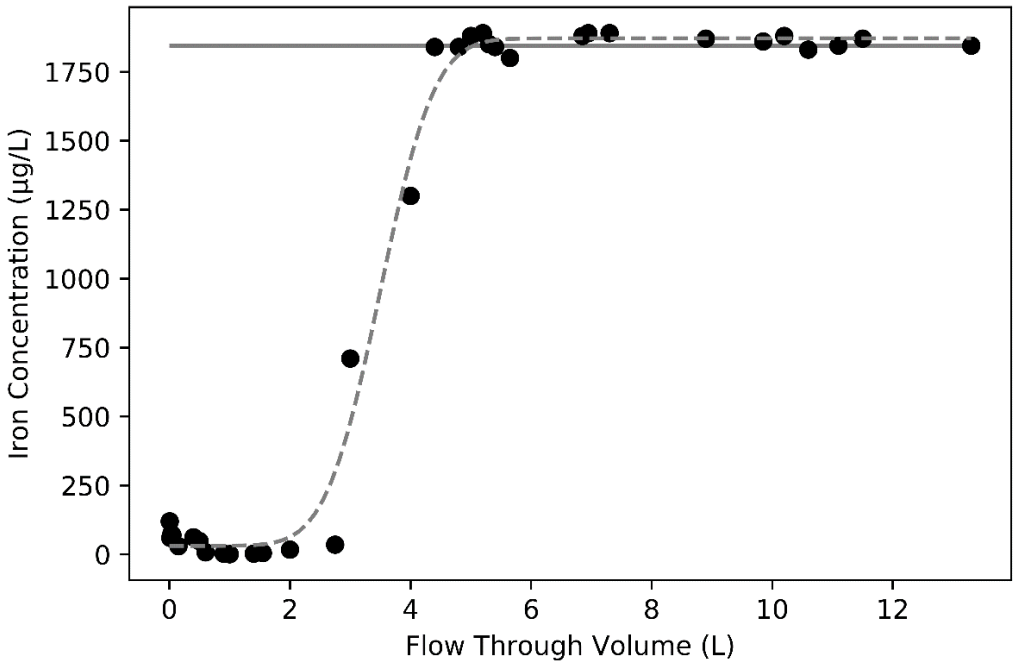

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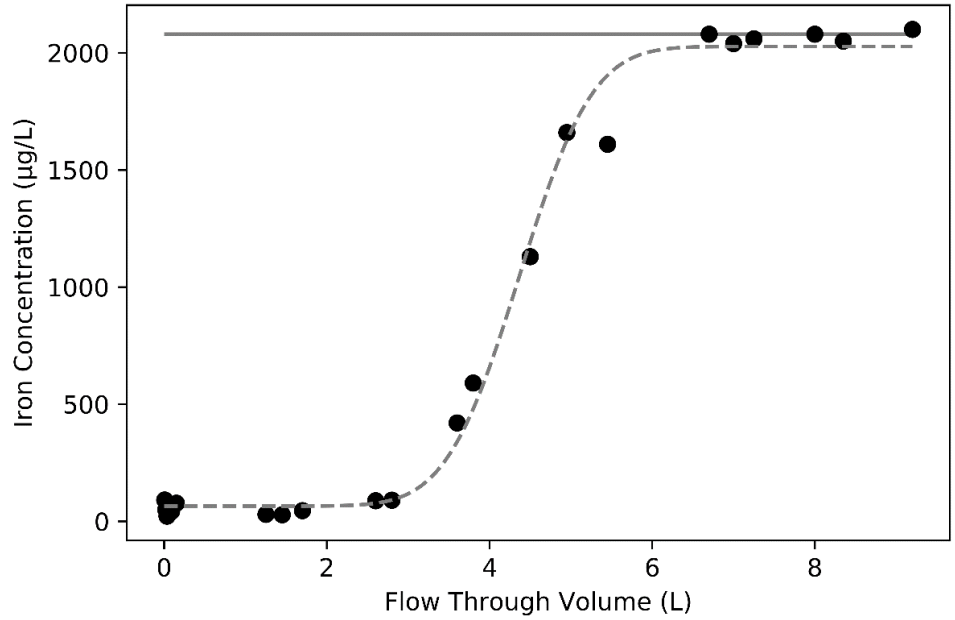

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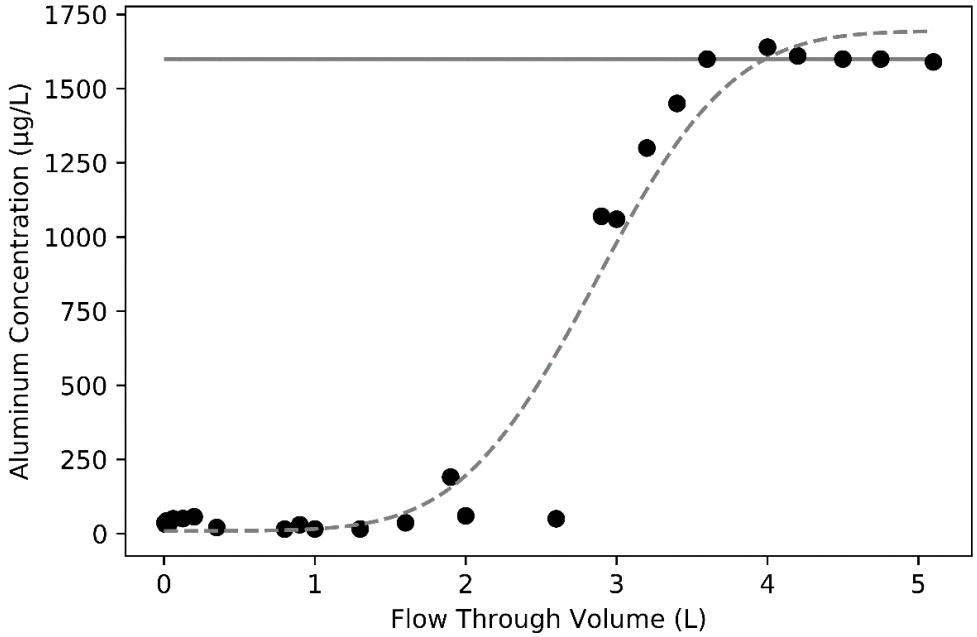

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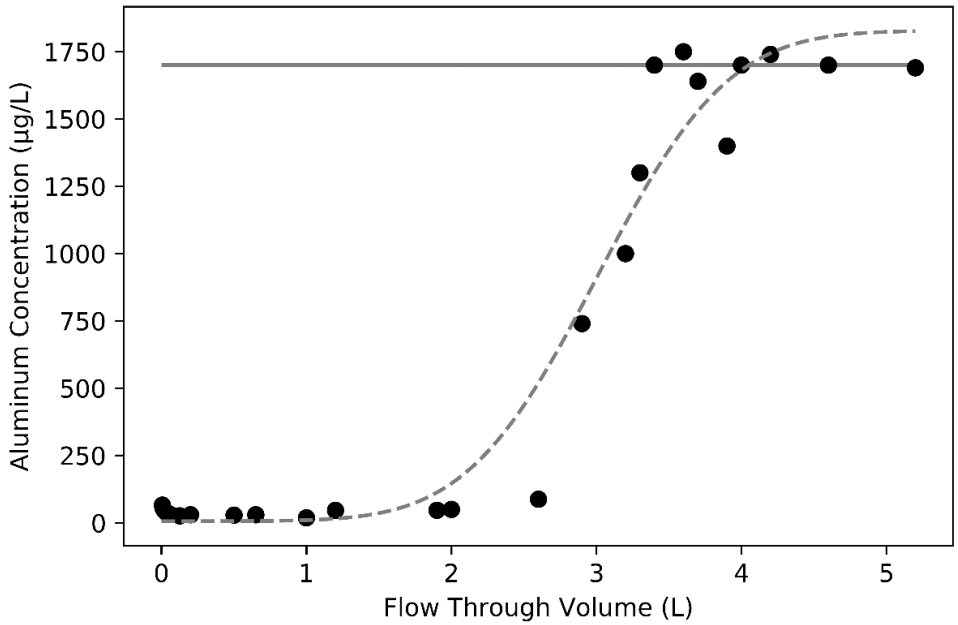

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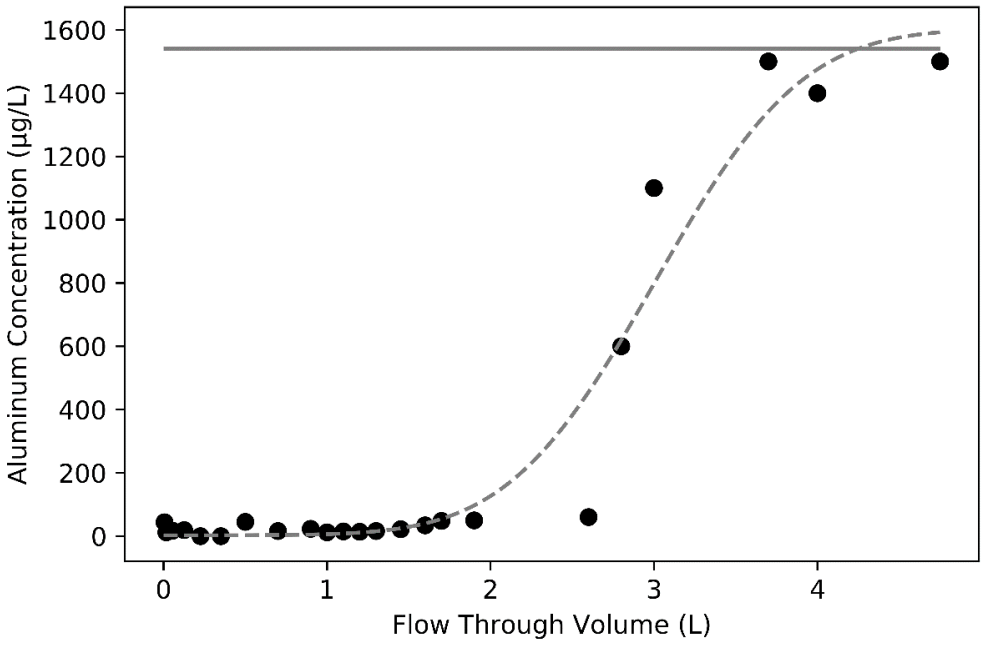

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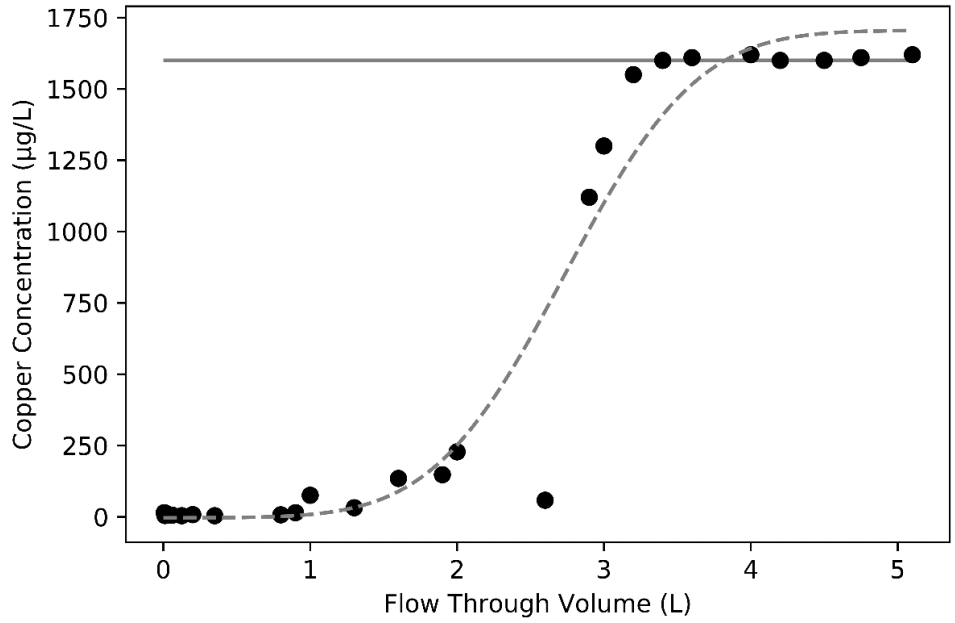

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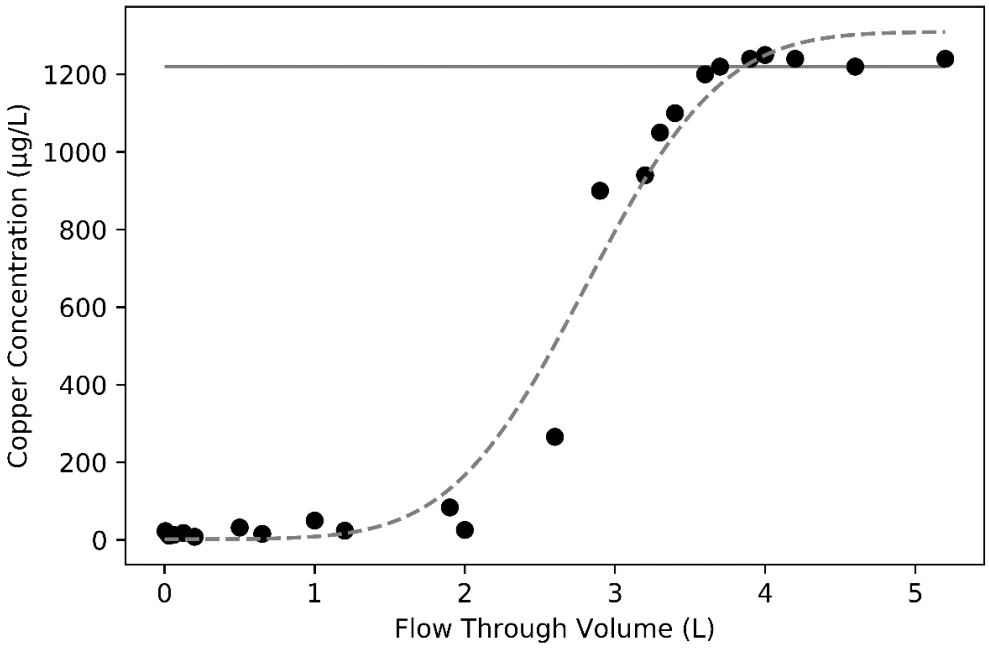

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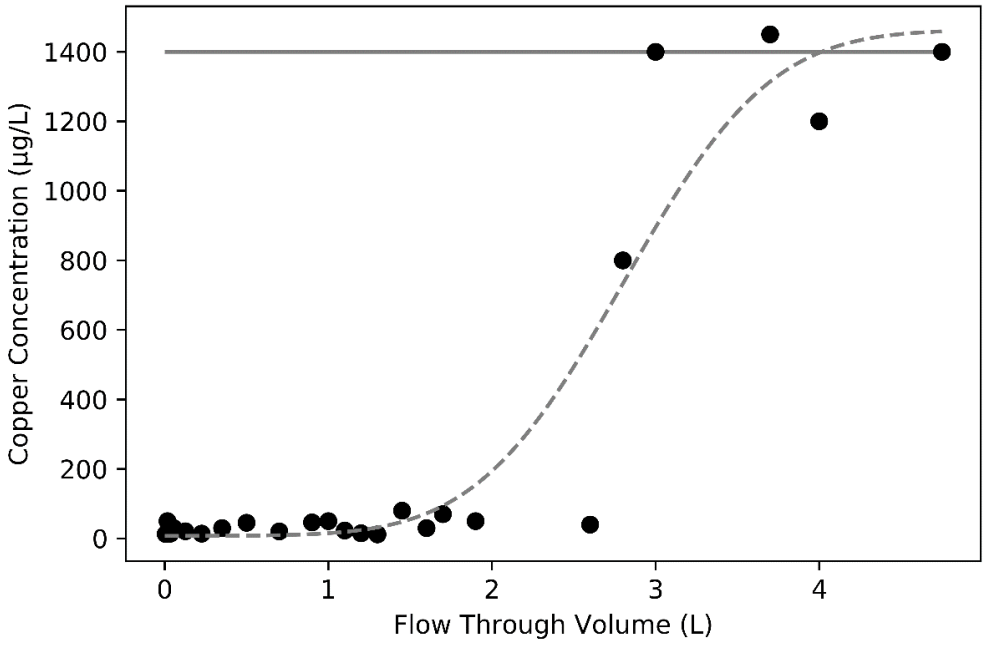

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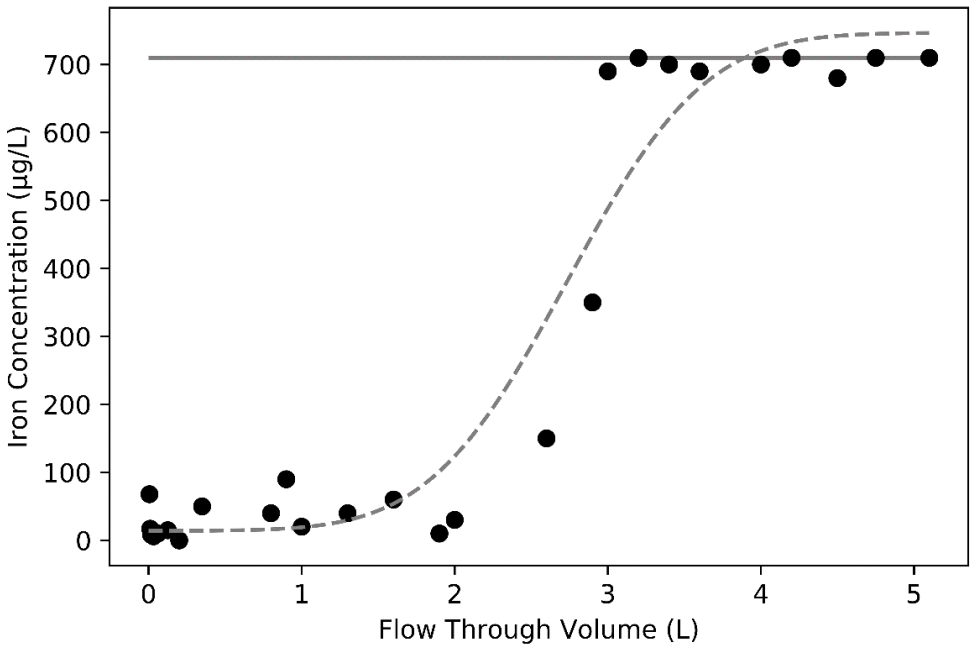

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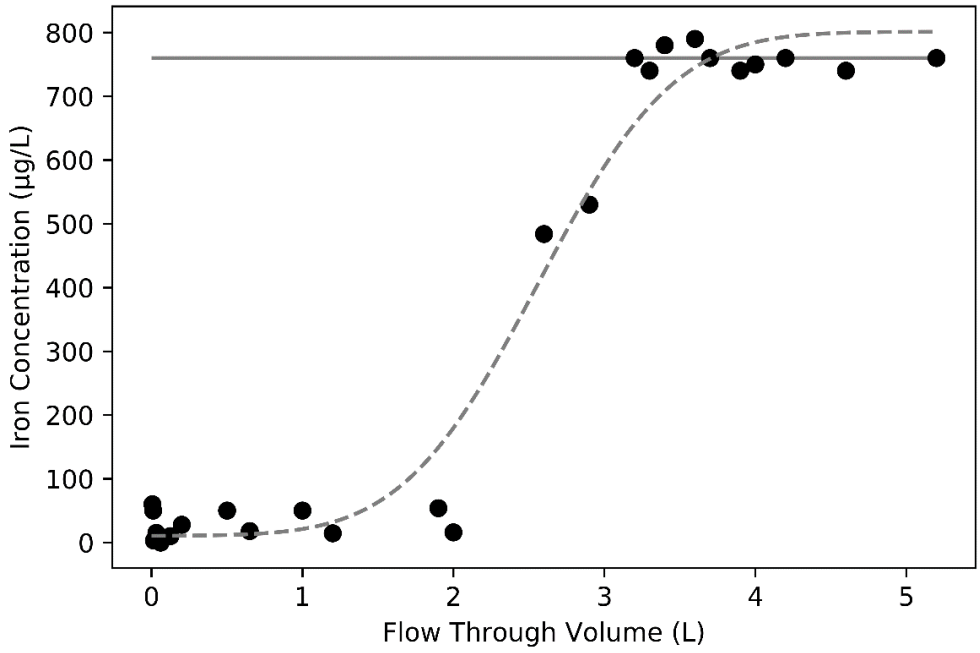

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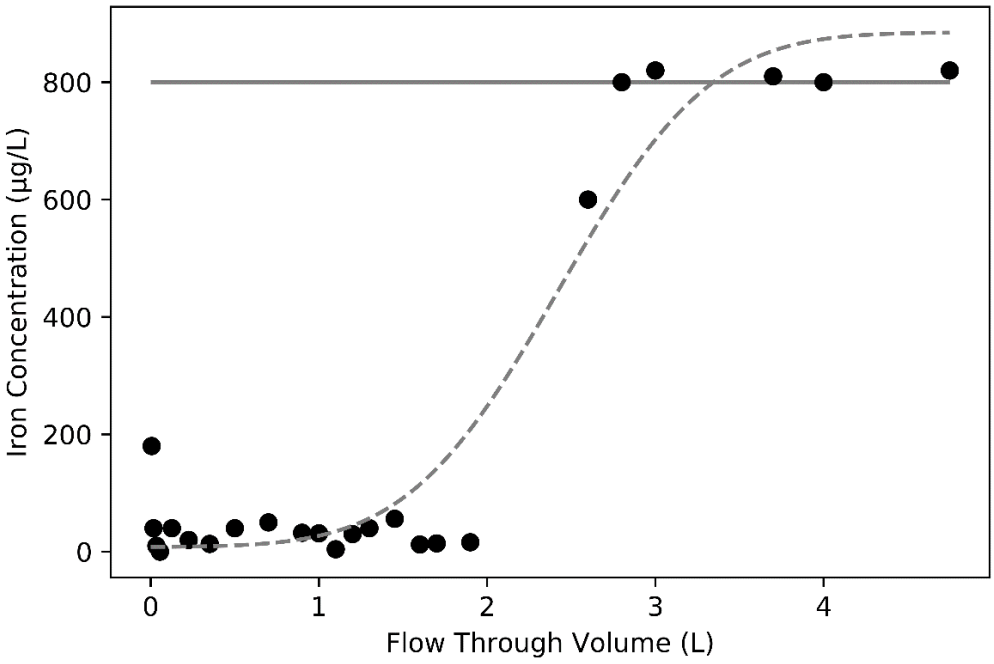

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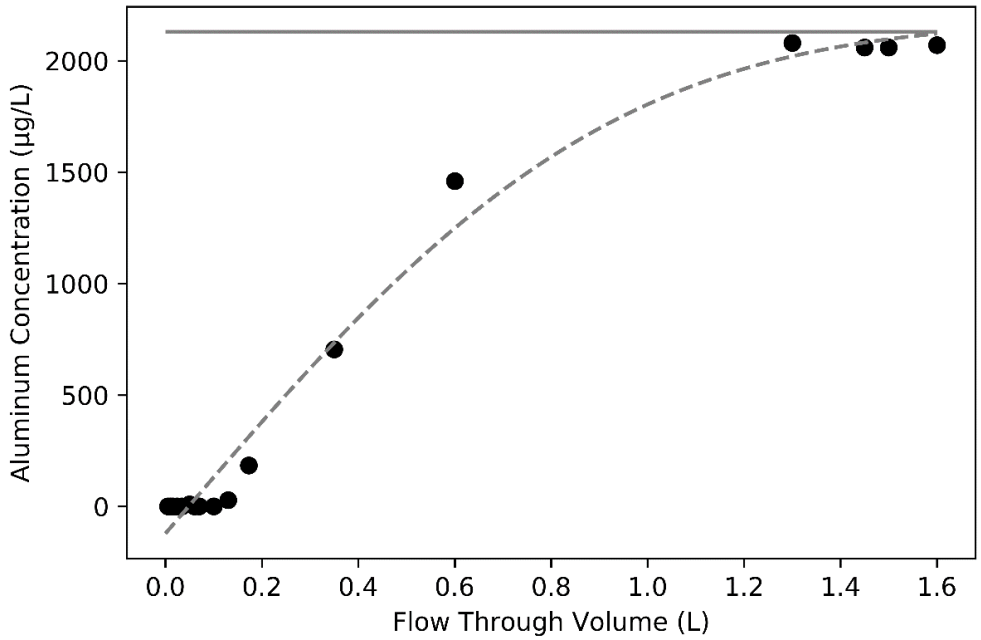

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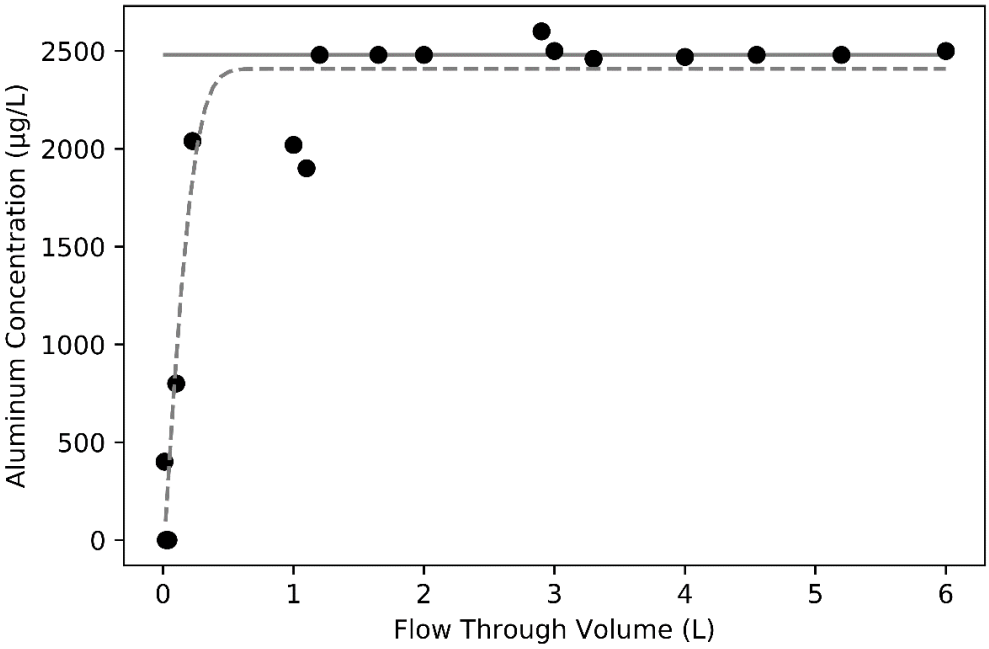

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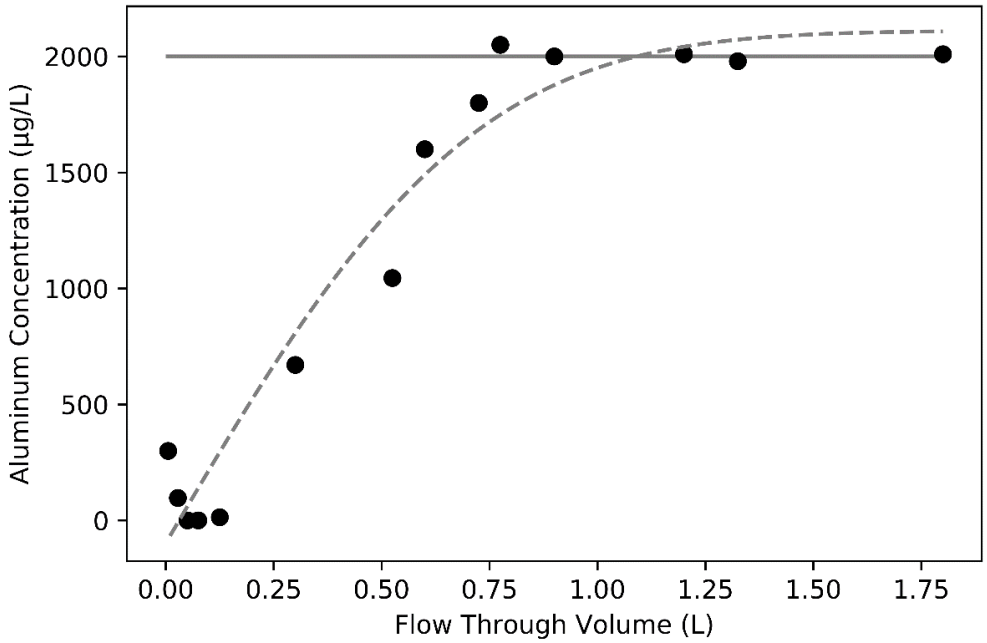

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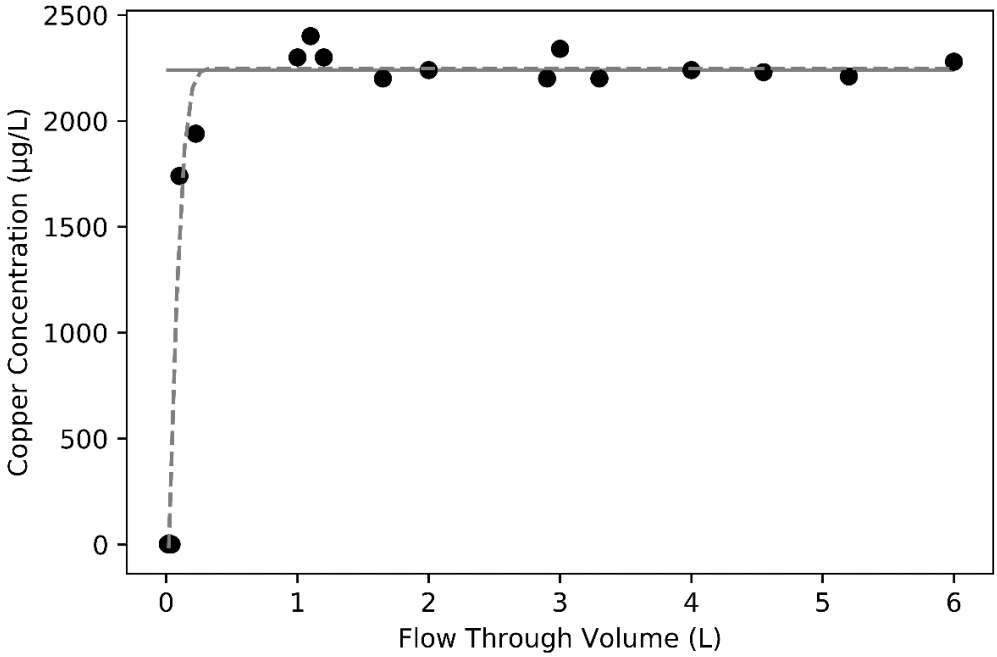

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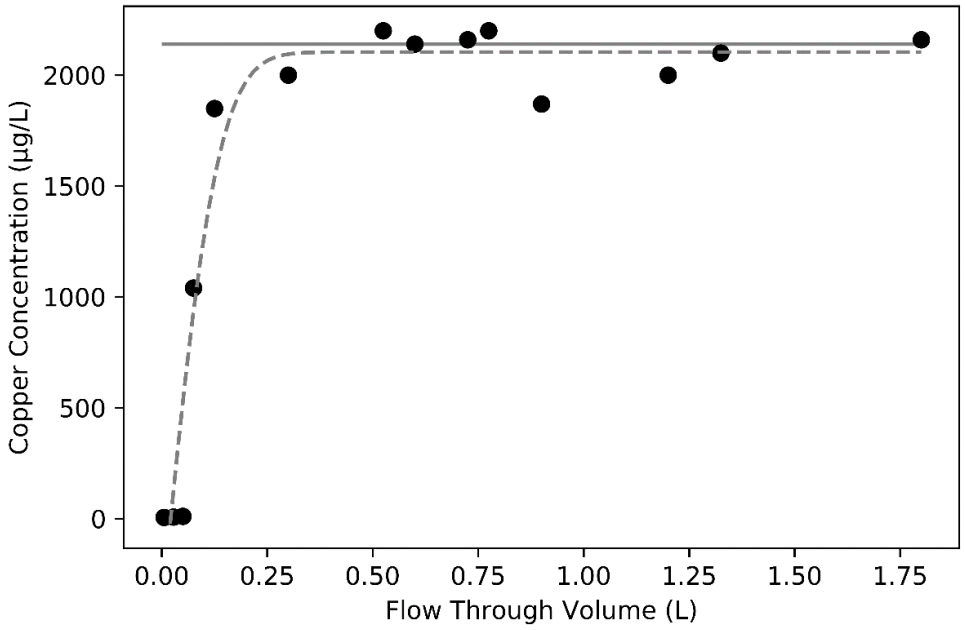

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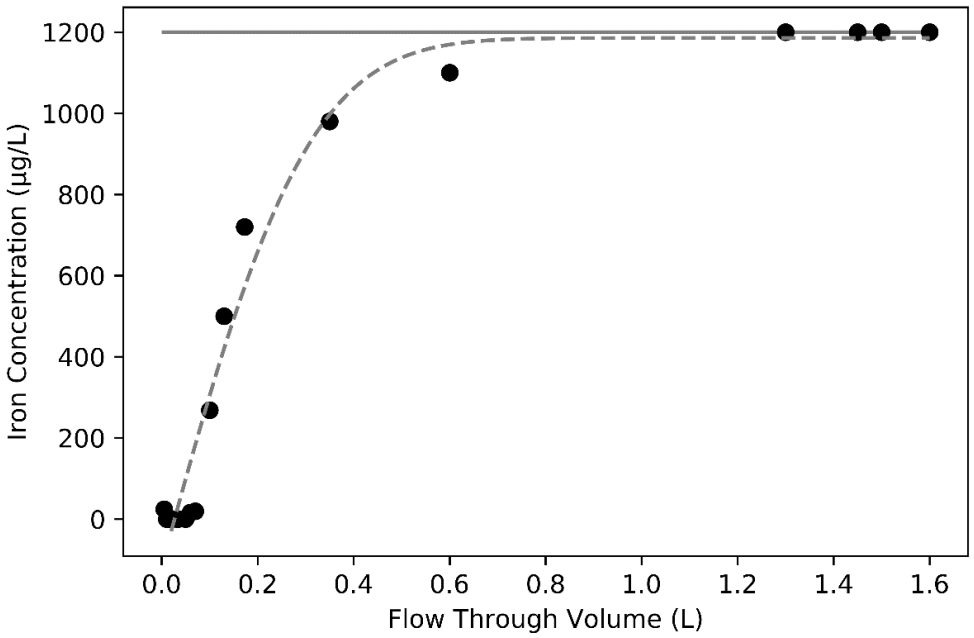

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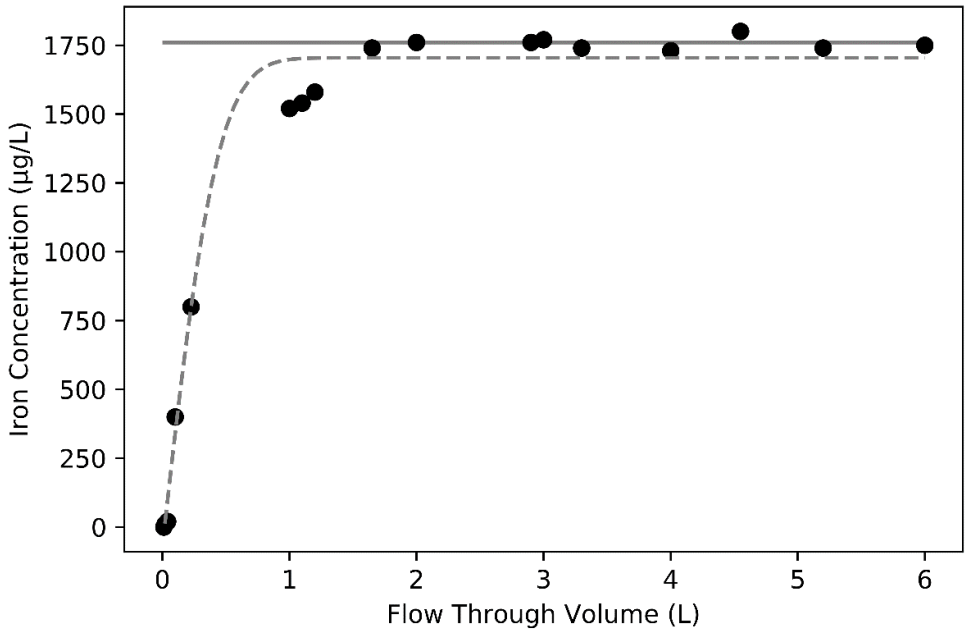

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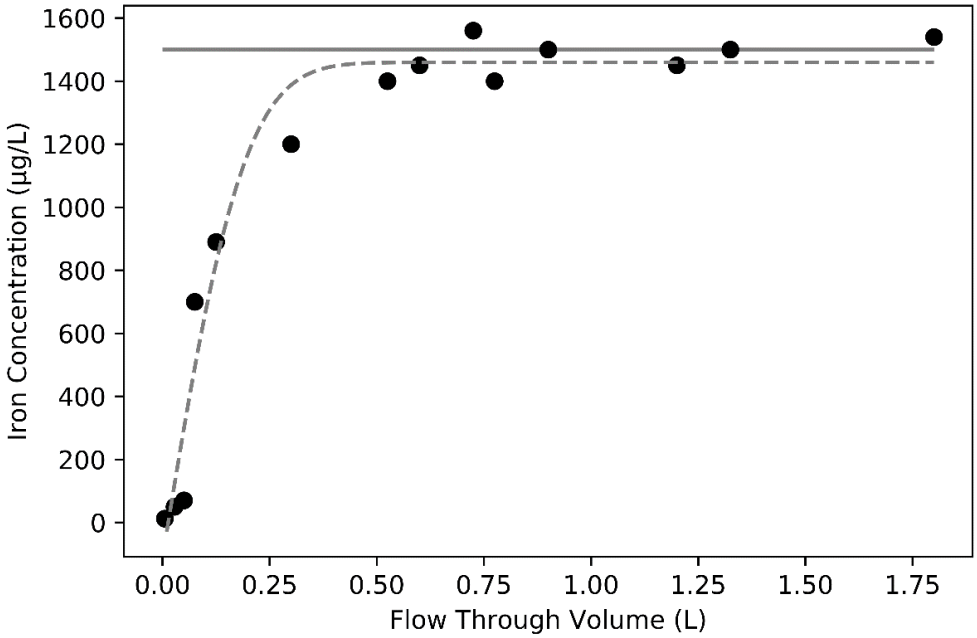

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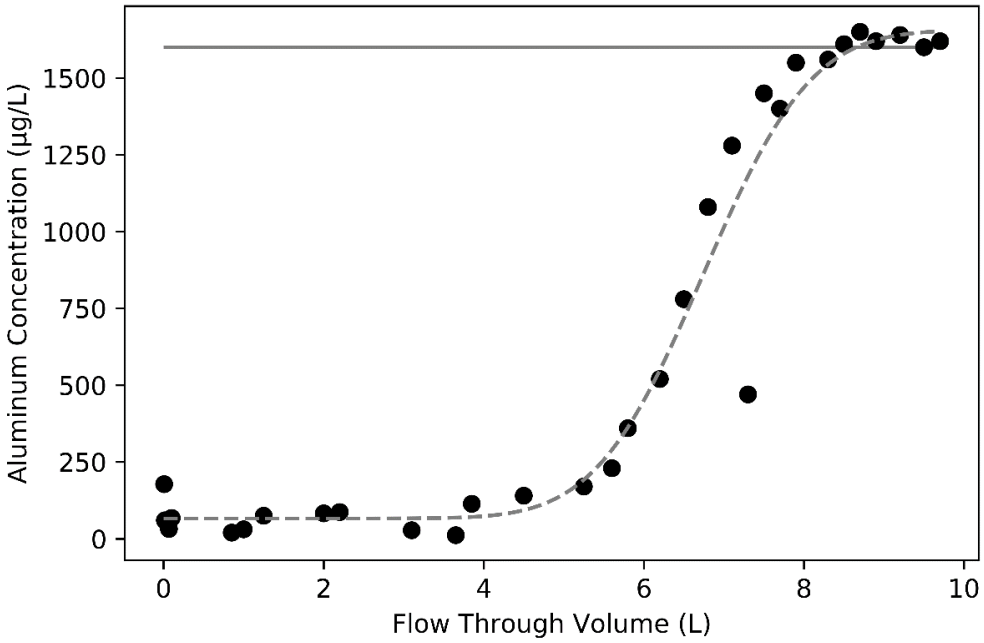

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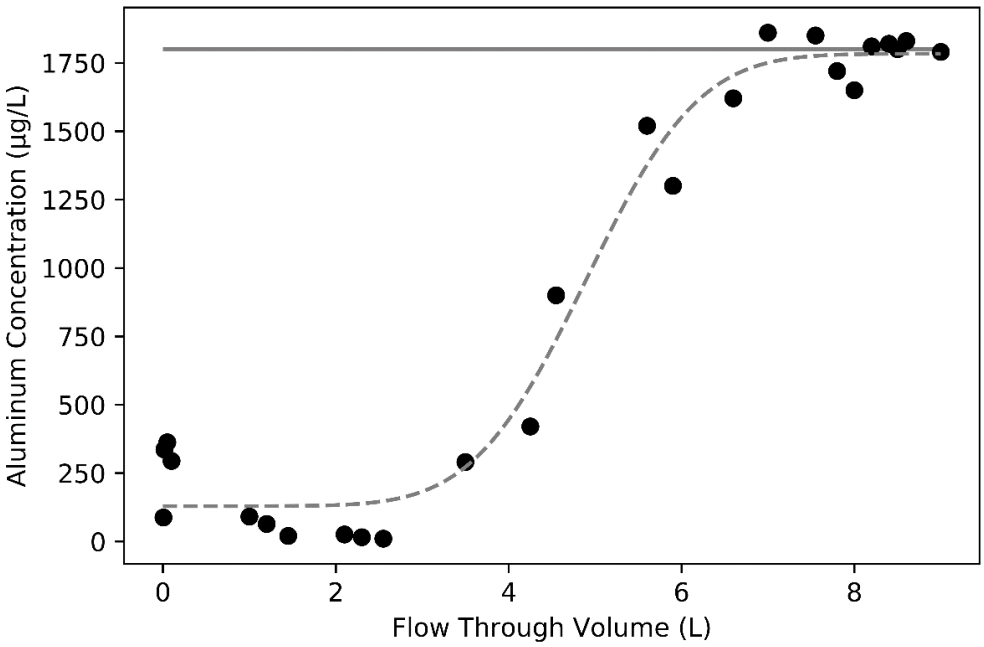

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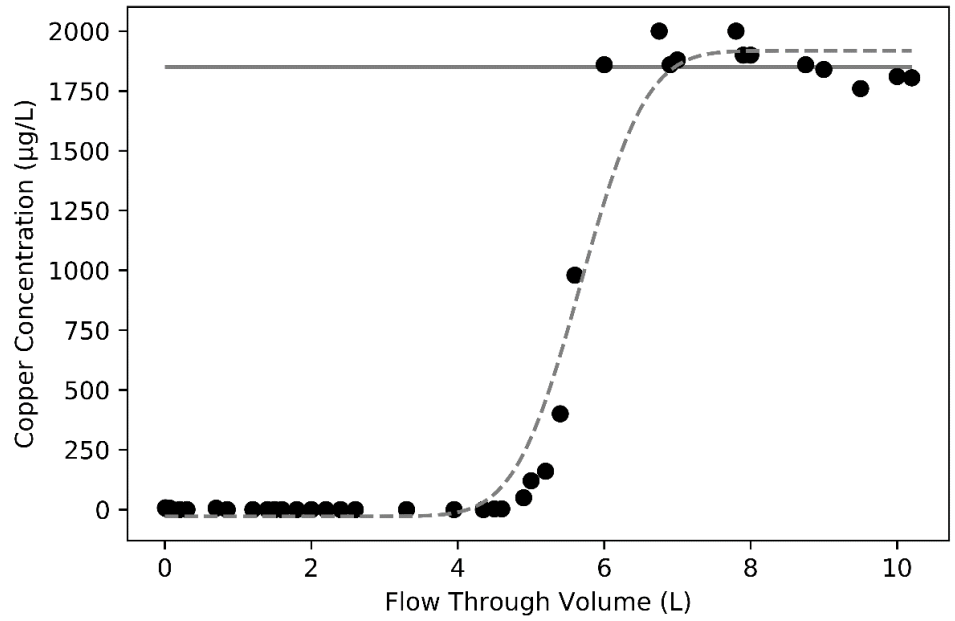

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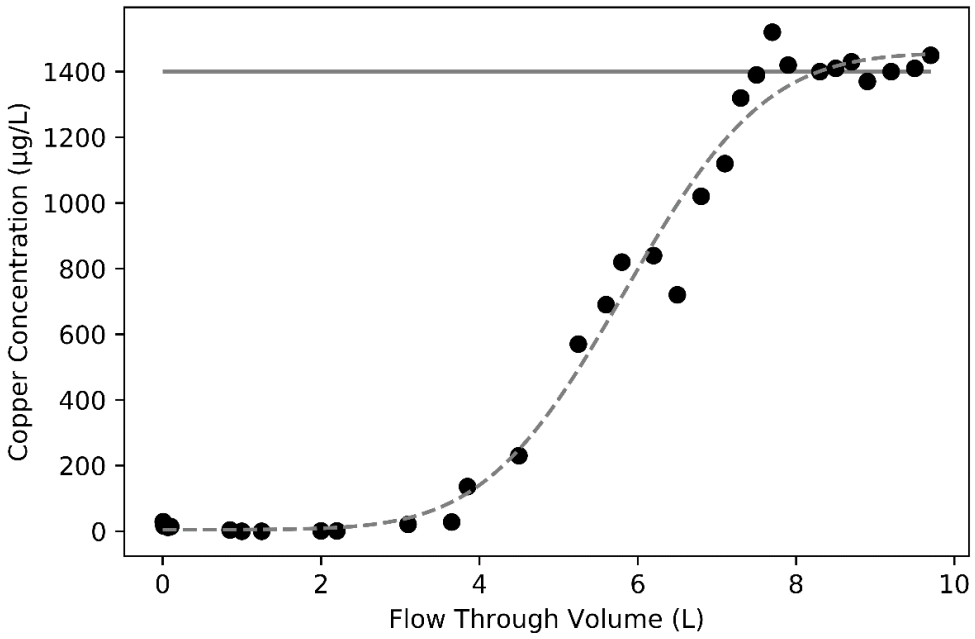

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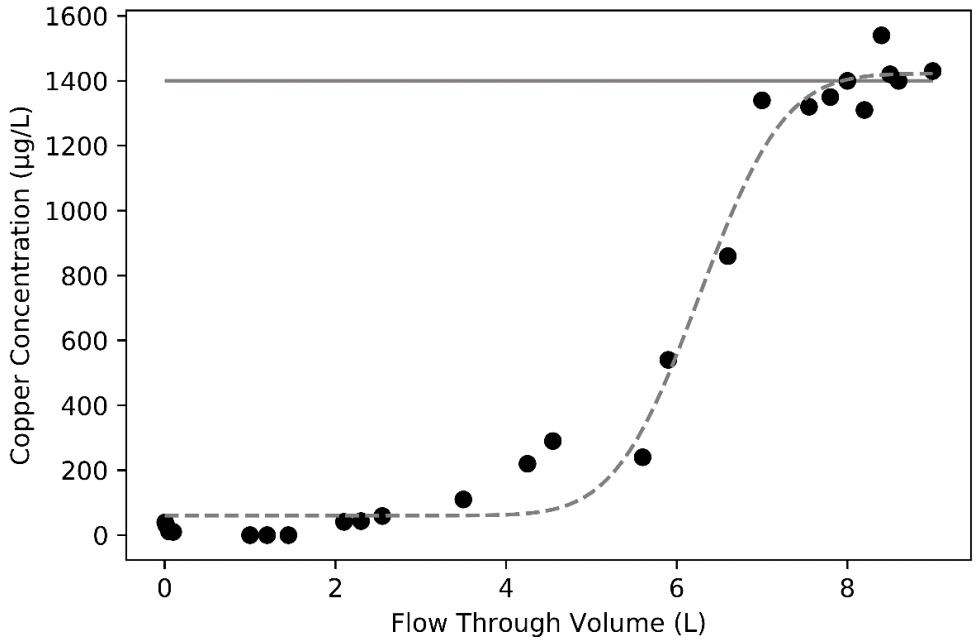

Figure 50. *Copper breakthrough compost column (3)*

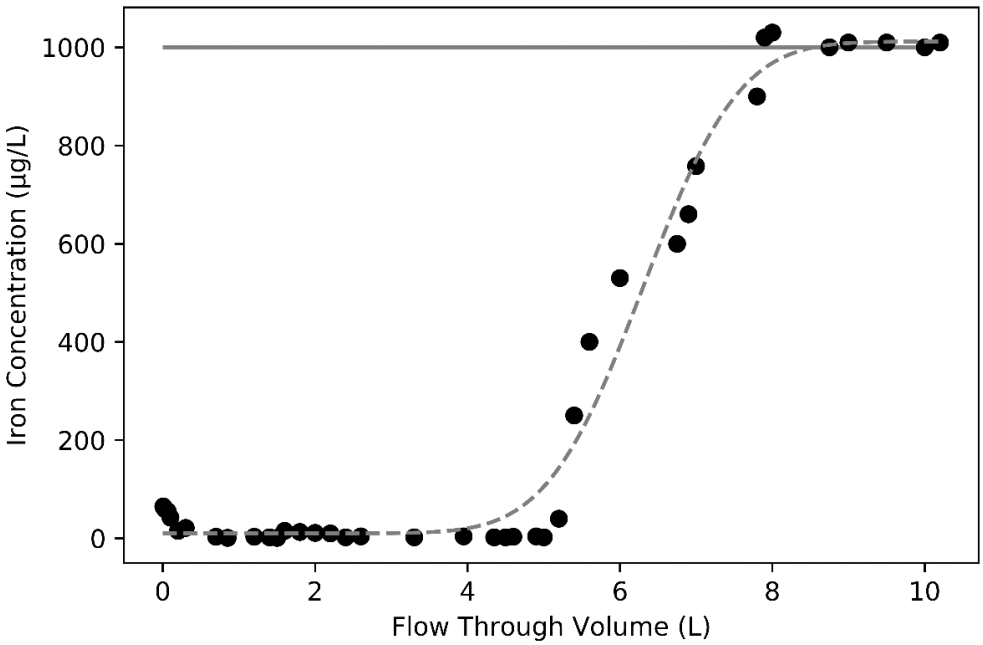

Figure 51. *Iron breakthrough compost column (1)*

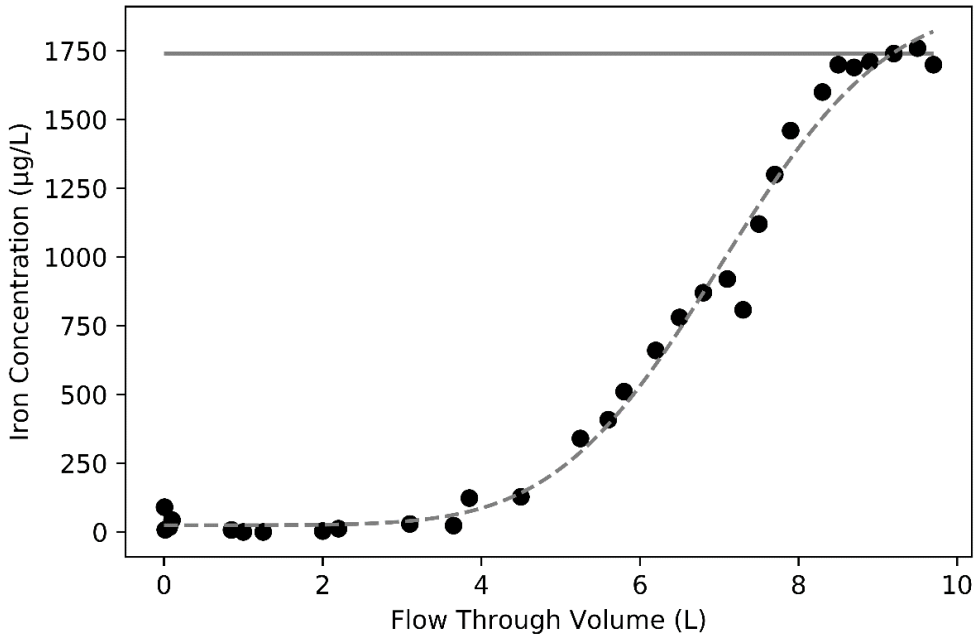

Figure 52. *Iron breakthrough compost column (2)*

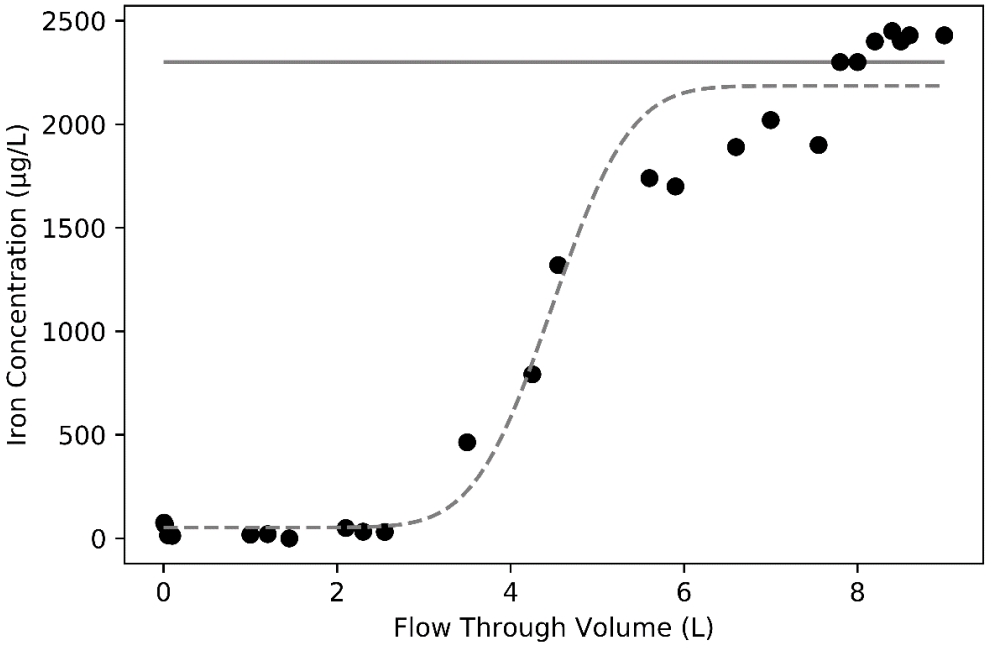

Figure 53. *Iron breakthrough compost column (3)*

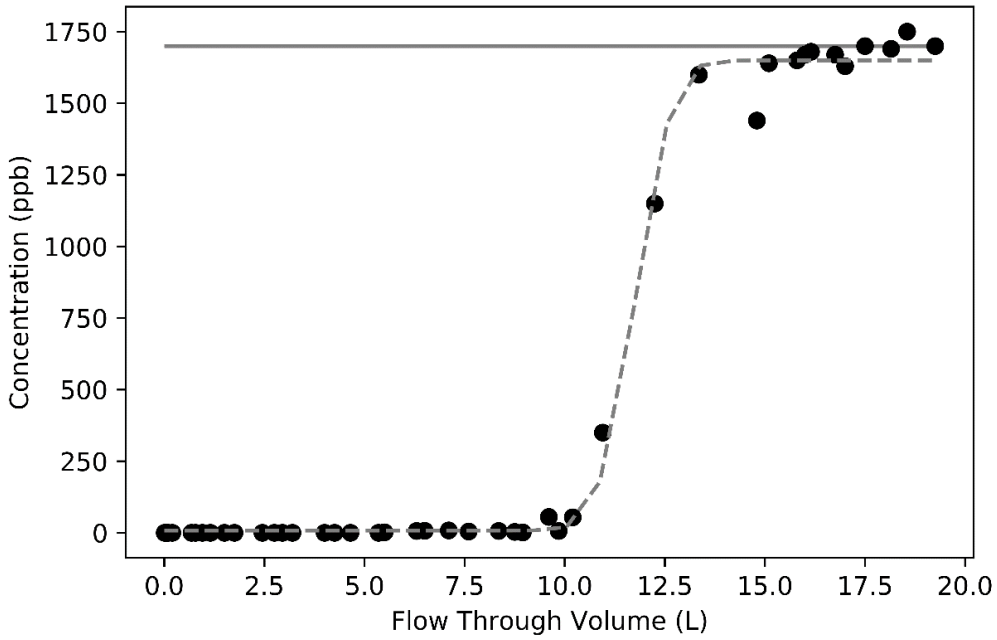

Figure 54. *Aluminum breakthrough marble column (2)*

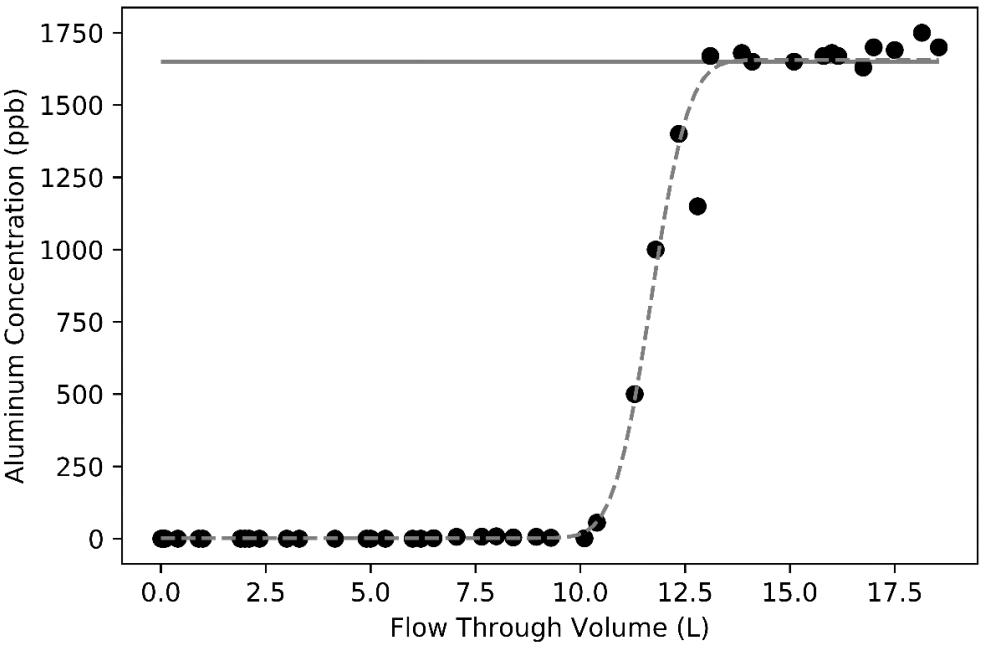

Figure 55. *Aluminum breakthrough marble column (3)*

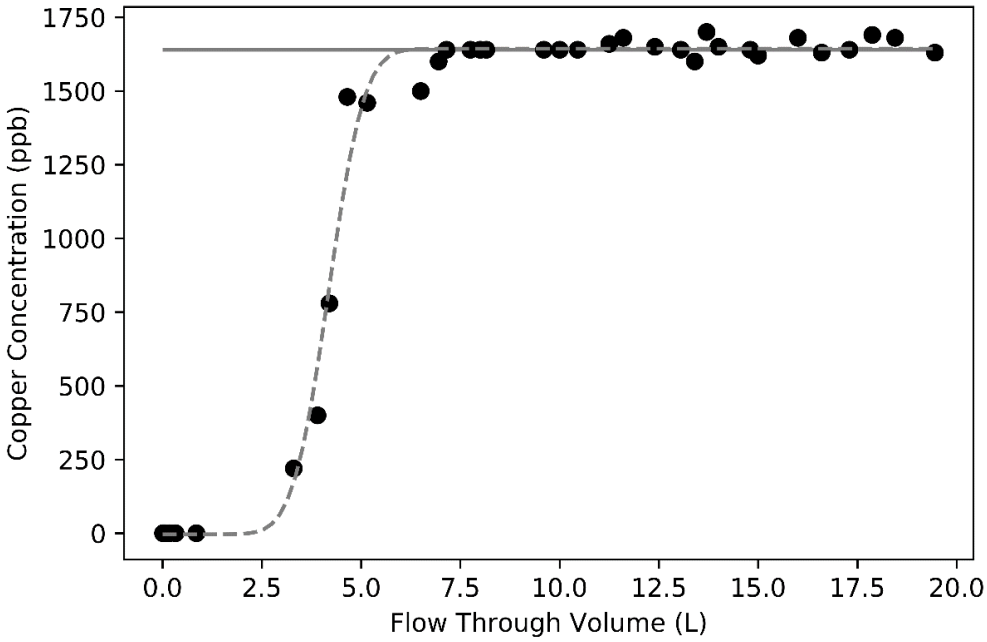

Figure 56. *Copper breakthrough marble column (1)*

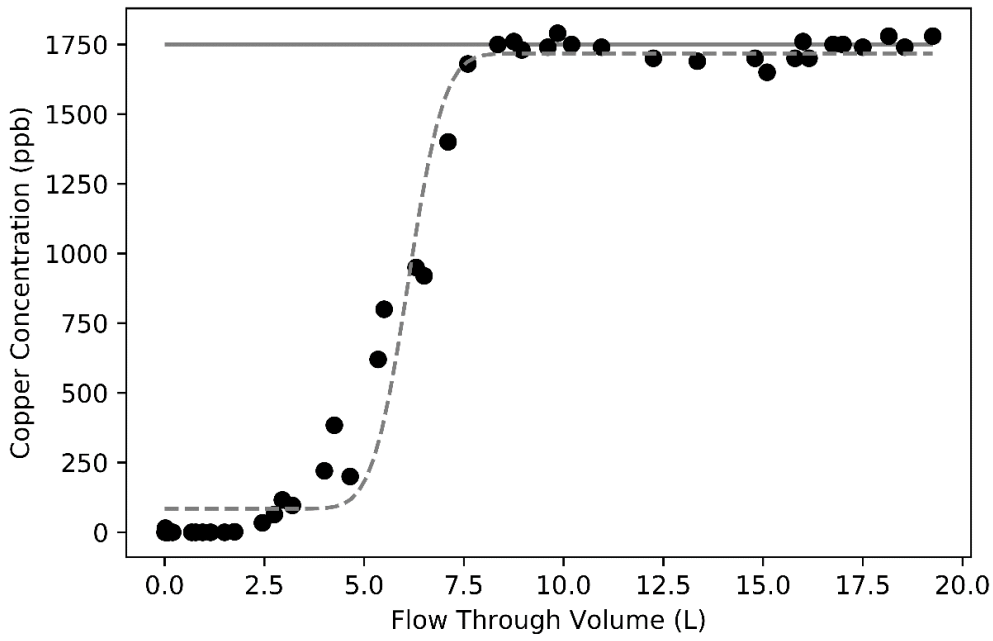

Figure 57. *Copper breakthrough marble column (2)*

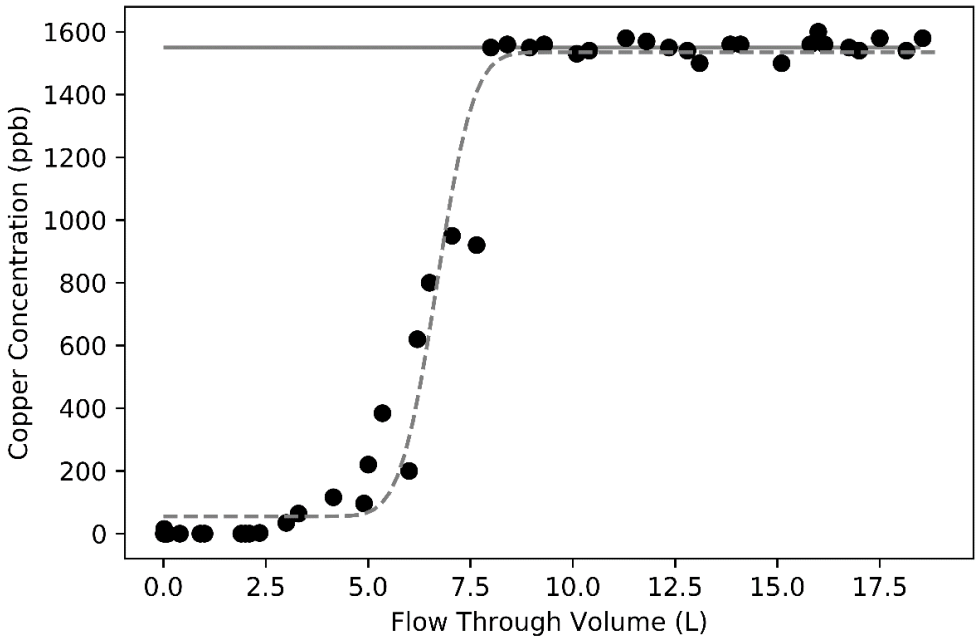

Figure 58. *Copper breakthrough marble column (3)*

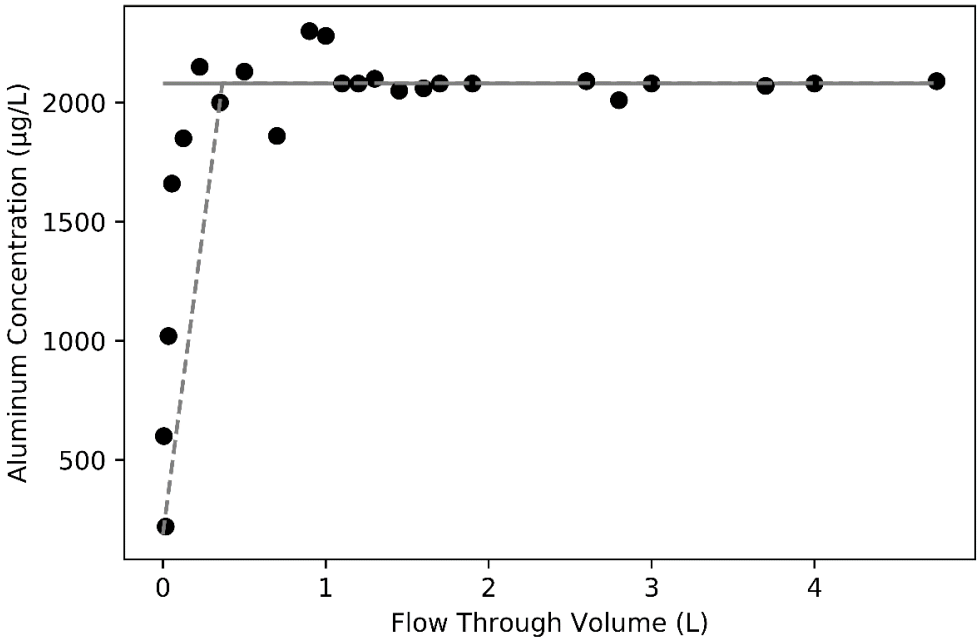

Figure 59. *Aluminum breakthrough sand column (1)*

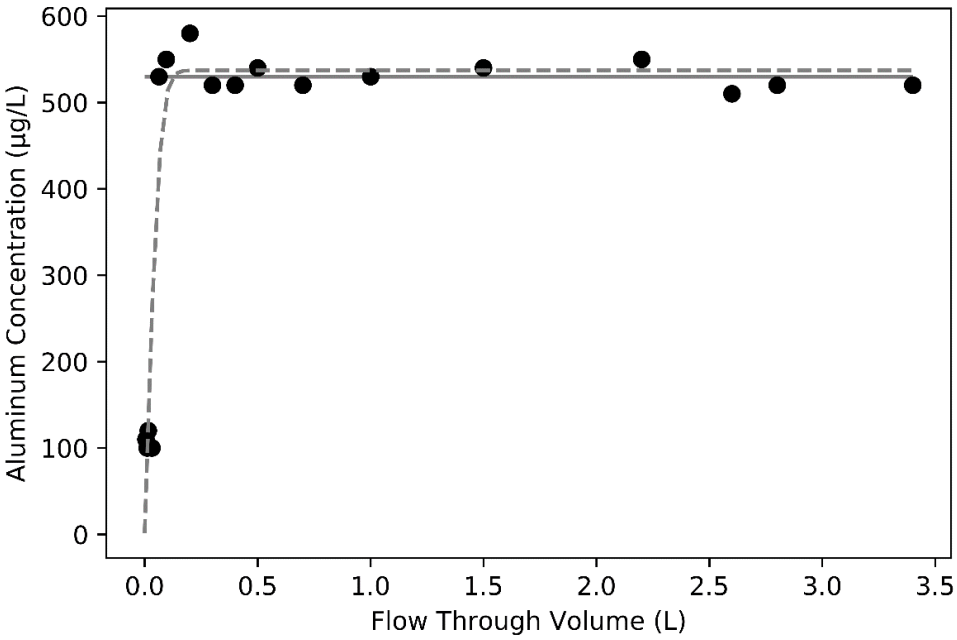

Figure 60. *Aluminum breakthrough sand column (2)*

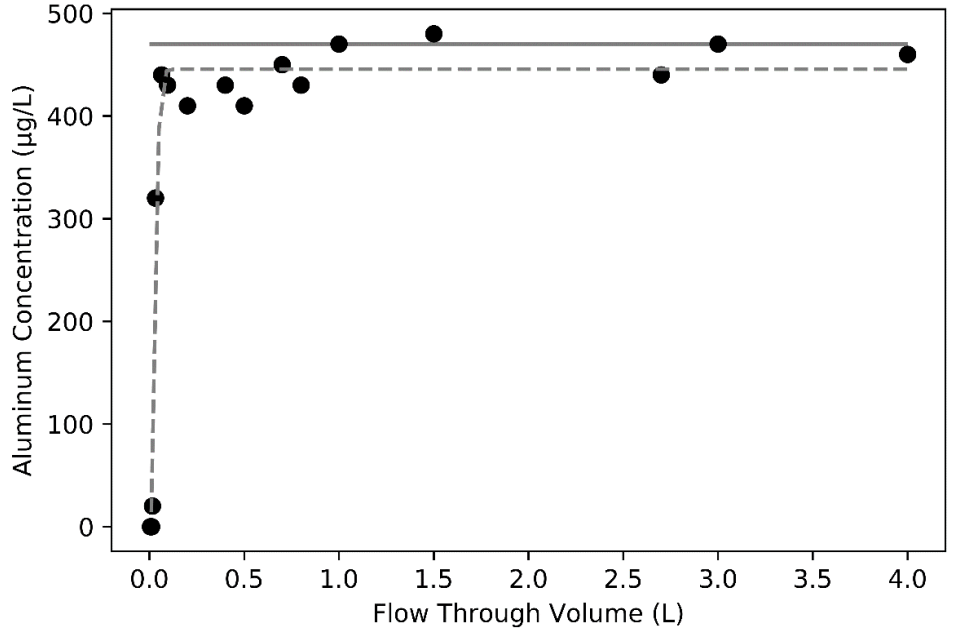

Figure 61. *Aluminum breakthrough sand column (3)*

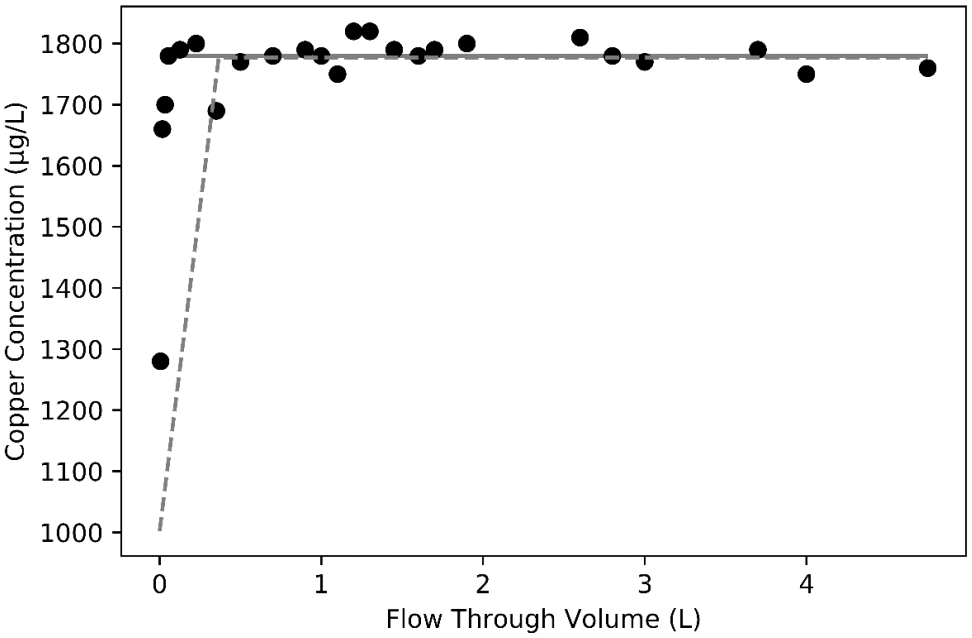

Figure 62. *Copper breakthrough sand column (1)*

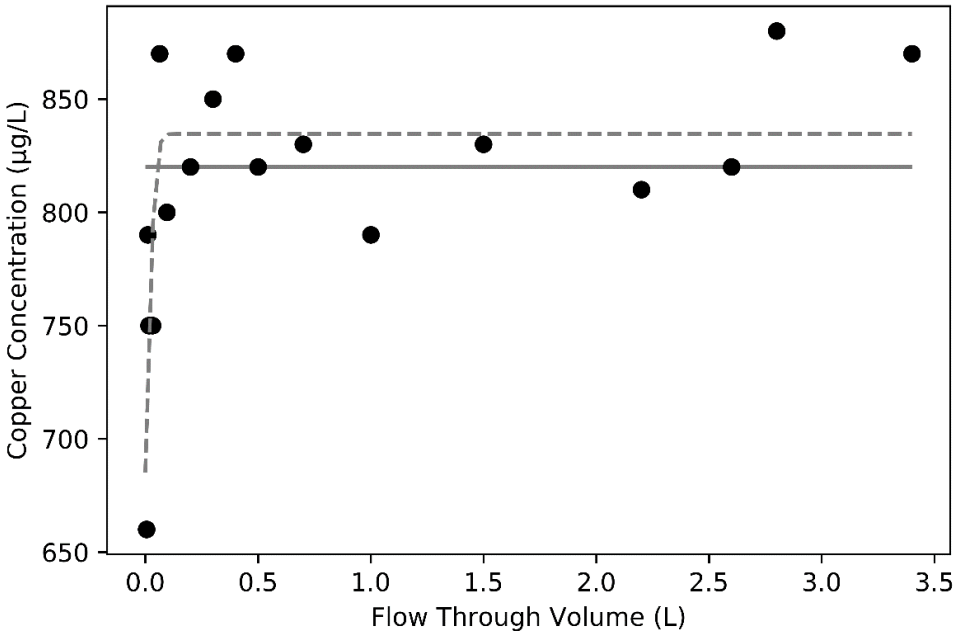

Figure 63. *Copper breakthrough sand column (2)*

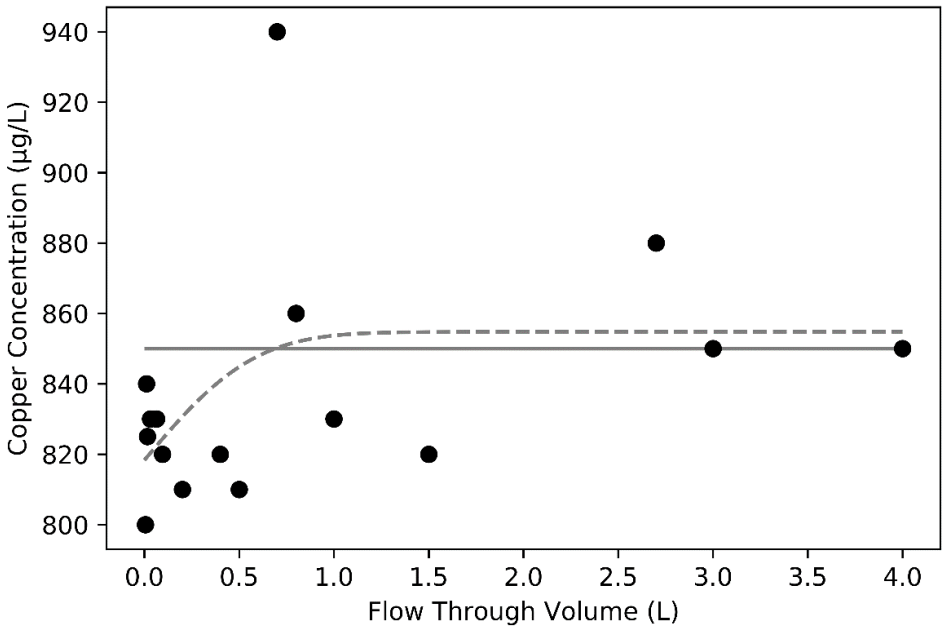

Figure 64. *Copper breakthrough sand column (3)*

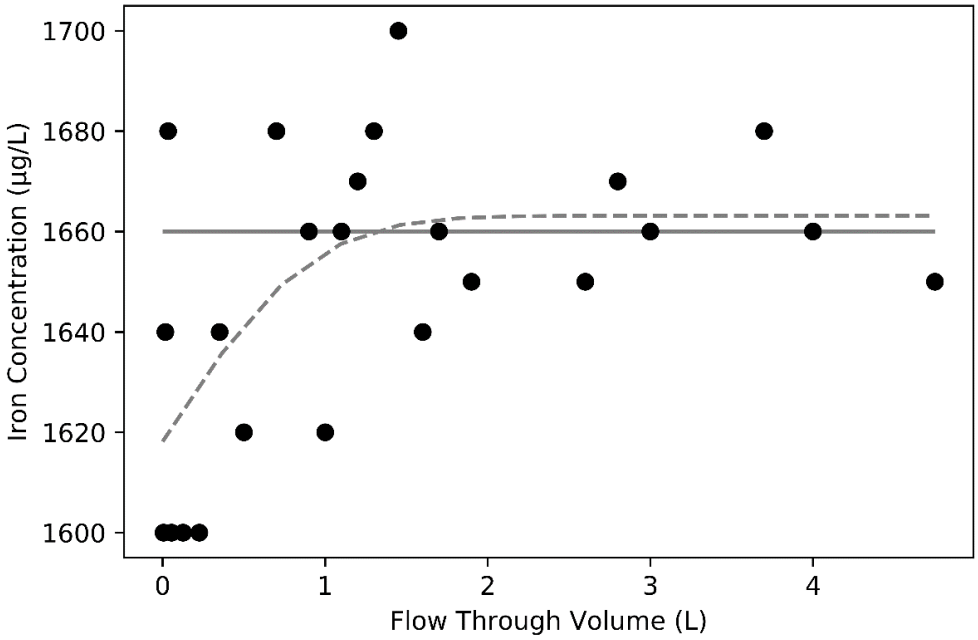

Figure 65. *Iron breakthrough sand column (1)*

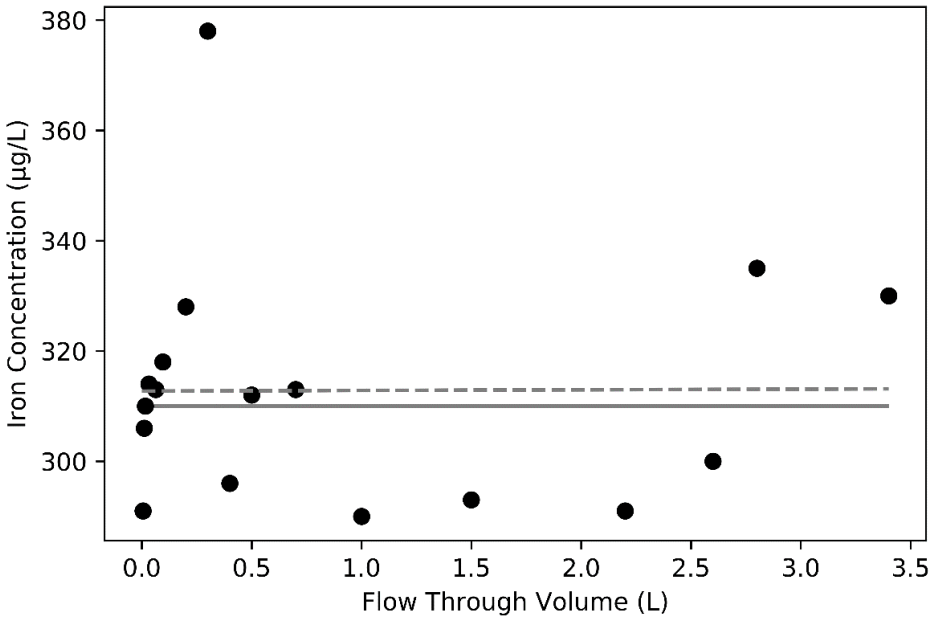

Figure 66. *Iron breakthrough sand column (2)*

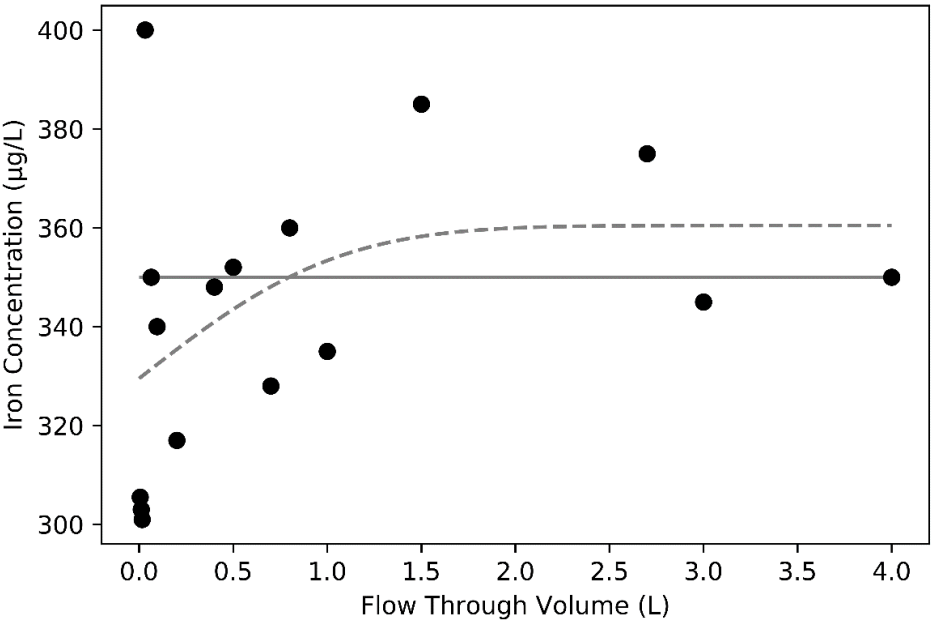

Figure 67. *Iron breakthrough sand column (3)*

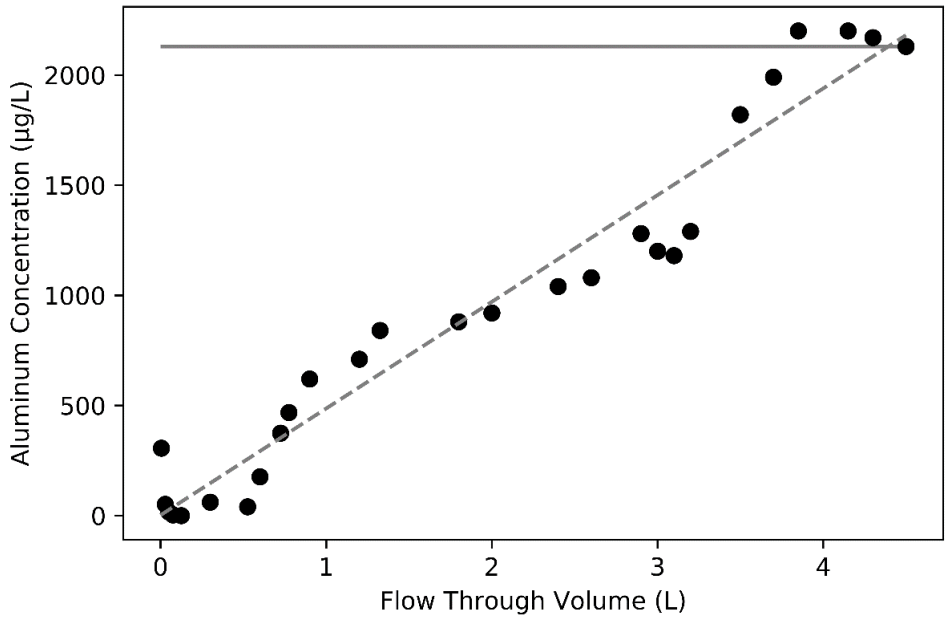

Figure 68. *Aluminum breakthrough vermiculite column (1)*

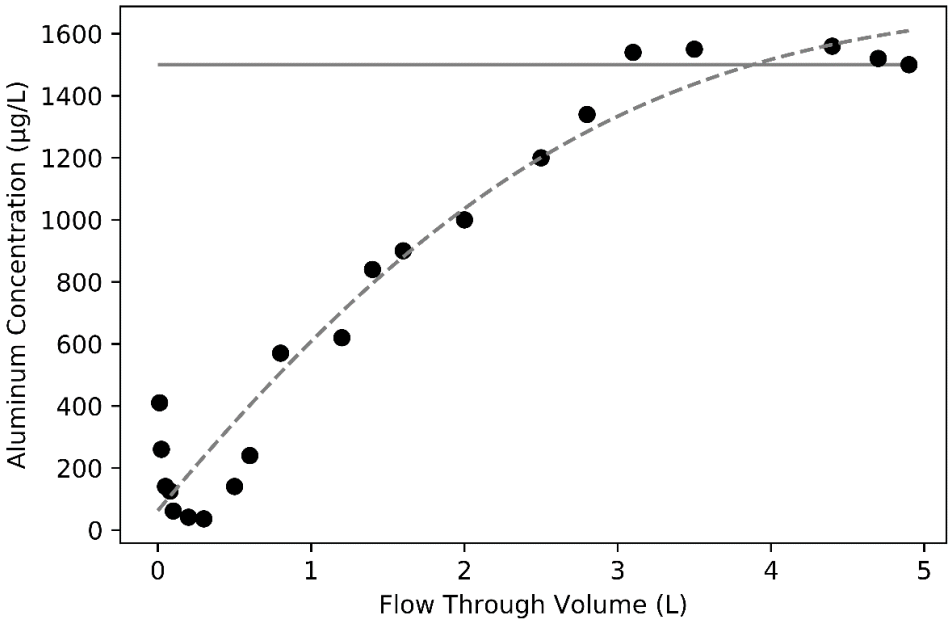

Figure 69. *Aluminum breakthrough vermiculite column (2)*

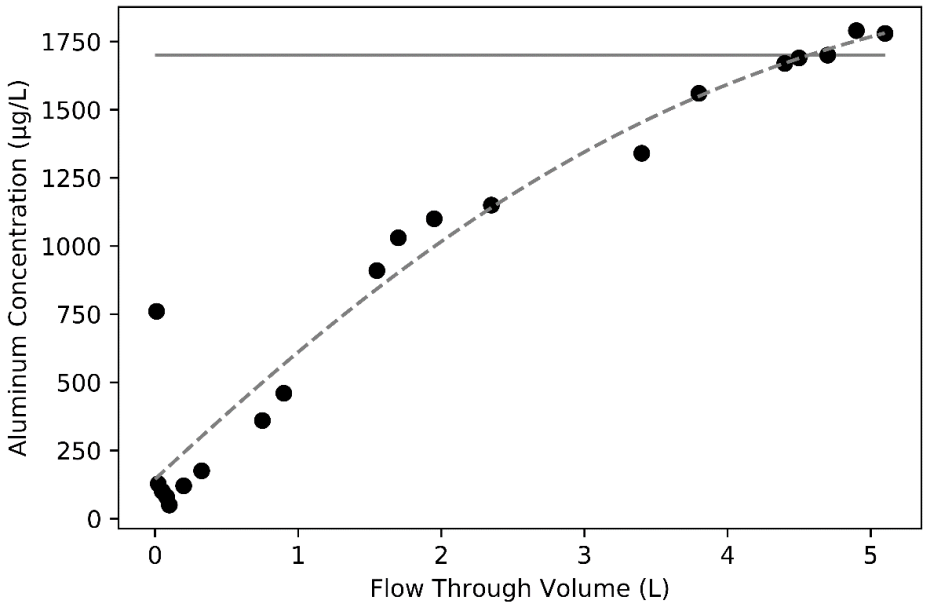

Figure 70. *Aluminum breakthrough vermiculite column (3)*

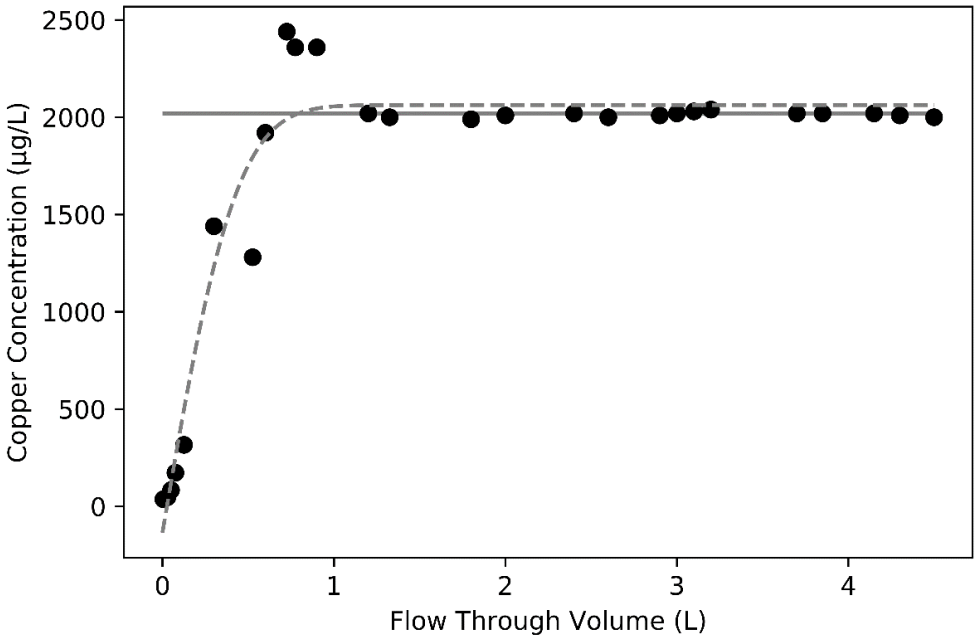

Figure 71. *Copper breakthrough vermiculite column (1)*

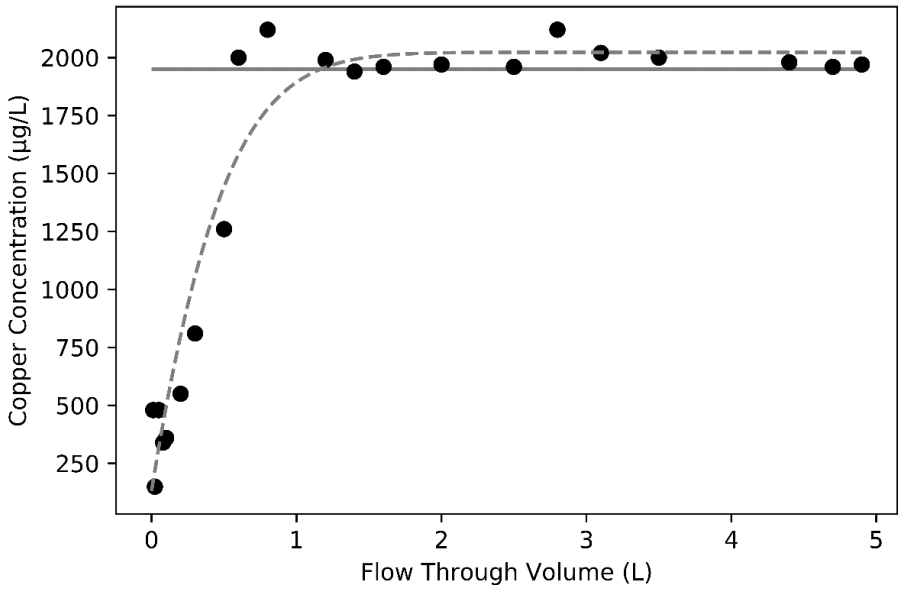

Figure 72. *Copper breakthrough vermiculite column (2)*

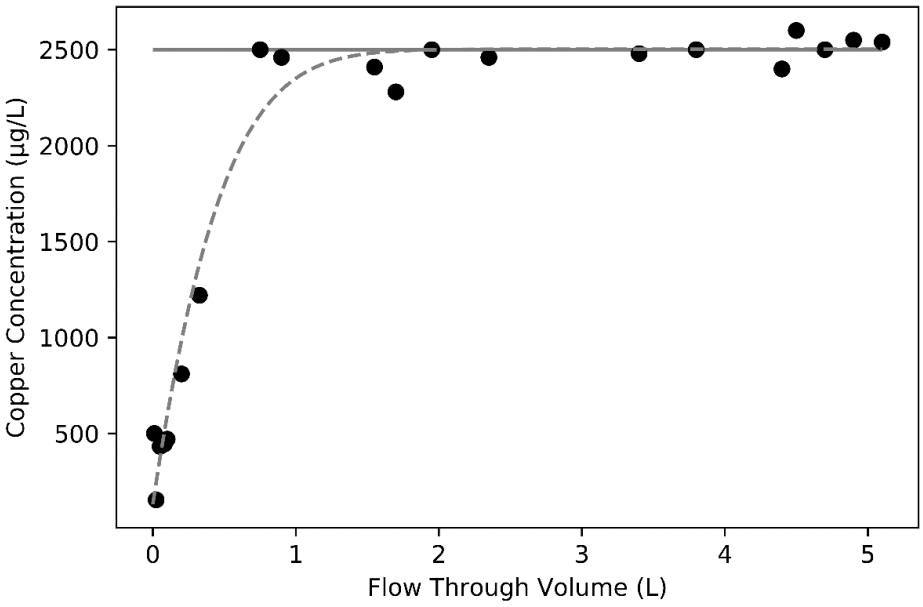

Figure 73. *Copper breakthrough vermiculite column (3)*

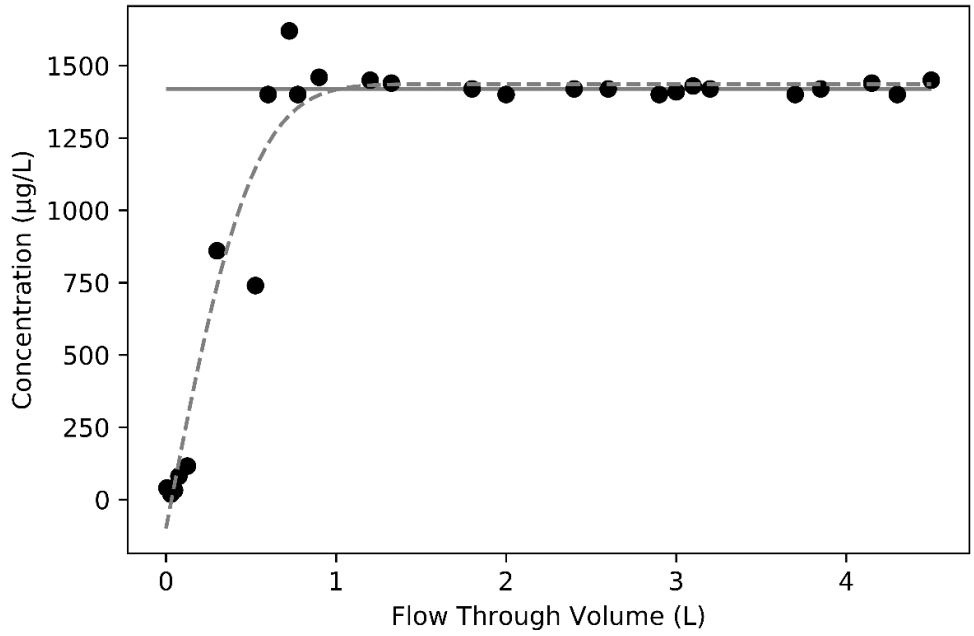

***Figure 74**. Iron breakthrough vermiculite column (1)*

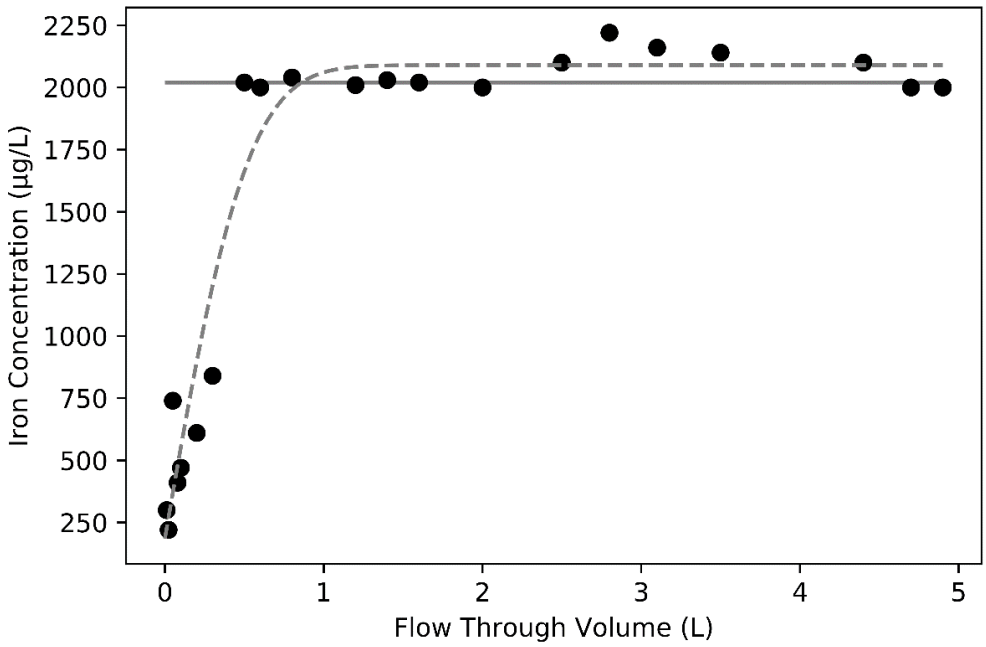

***Figure 75.** Iron breakthrough vermiculite column (2)*

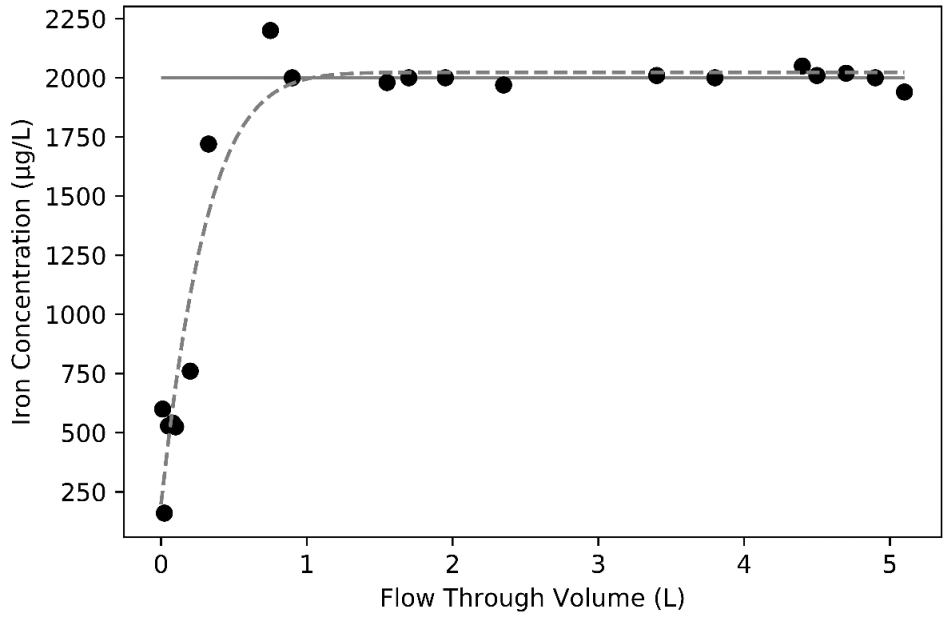

***Figure 76**. Iron breakthrough vermiculite column (3)*

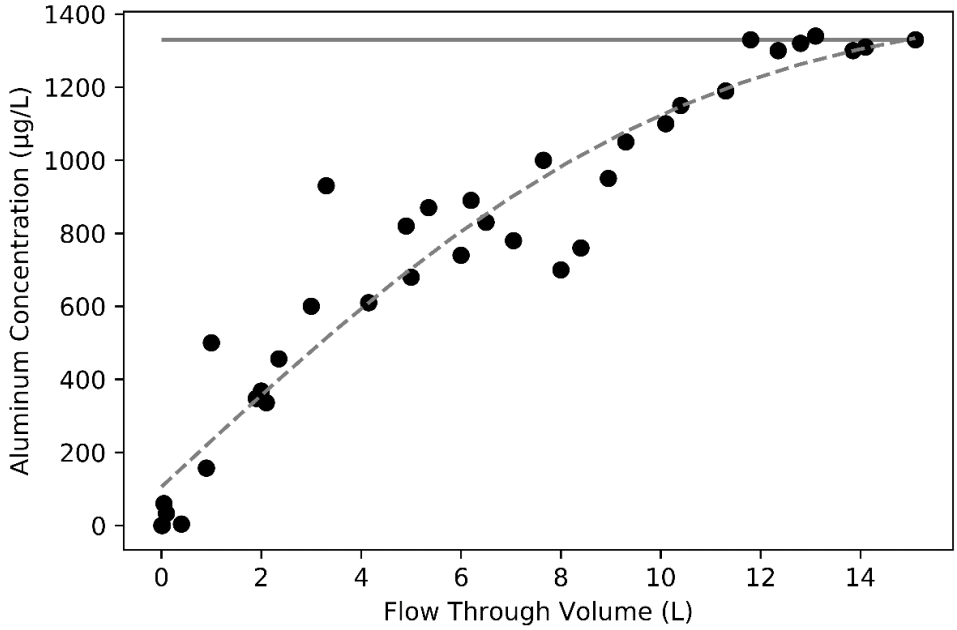

***Figure 77**. Aluminum breakthrough zeolite column (1)*

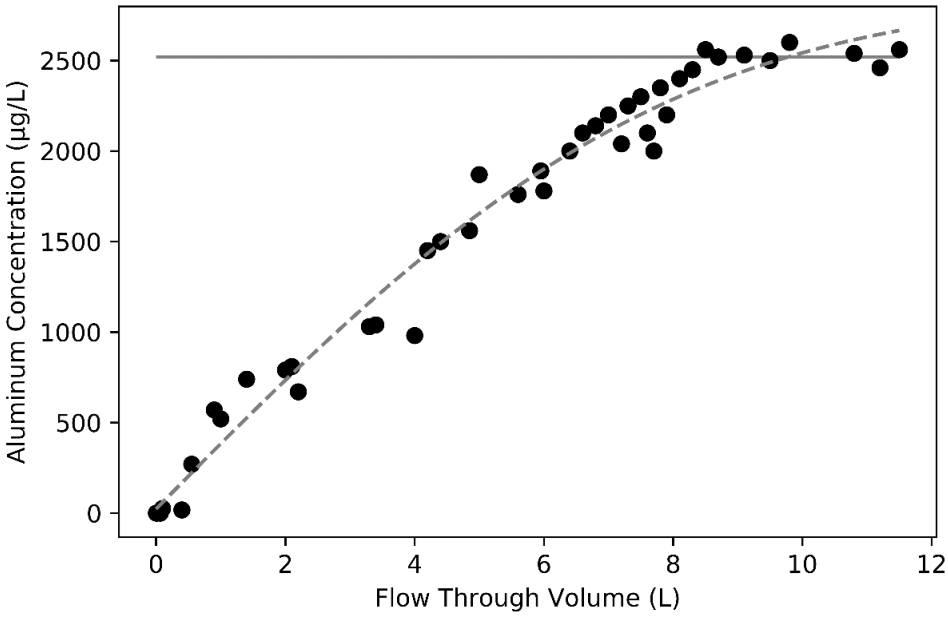

Figure 78. *Aluminum breakthrough zeolite column (2)*

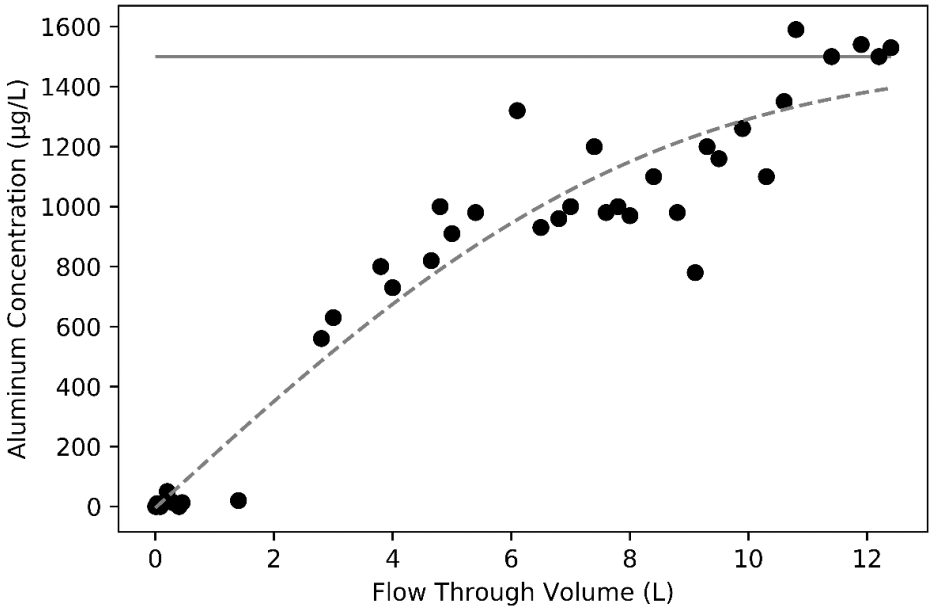

Figure 79. *Aluminum breakthrough zeolite column (3)*

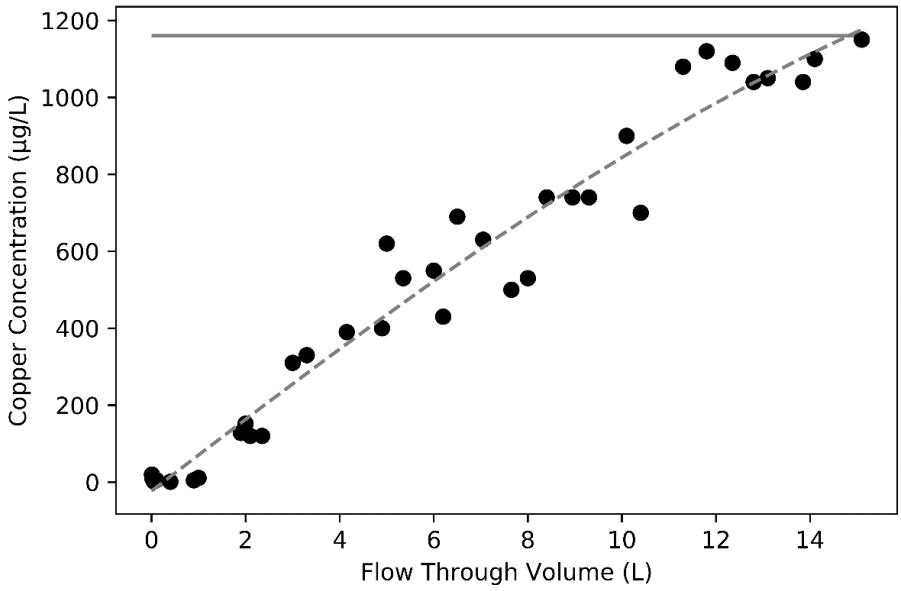

Figure 80. *Copper breakthrough zeolite column (1)*

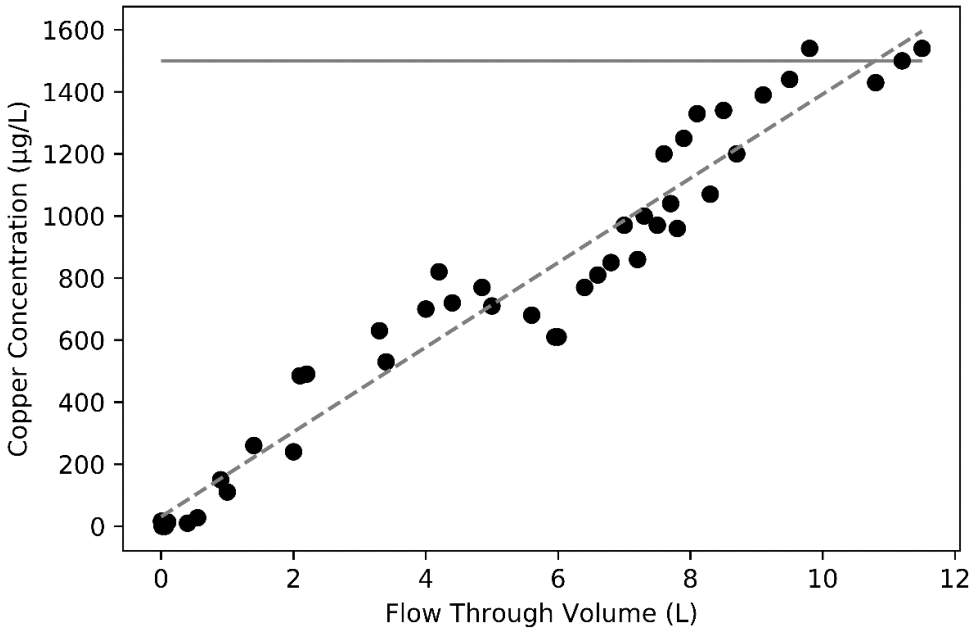

Figure 81. *Copper breakthrough zeolite column (2)*

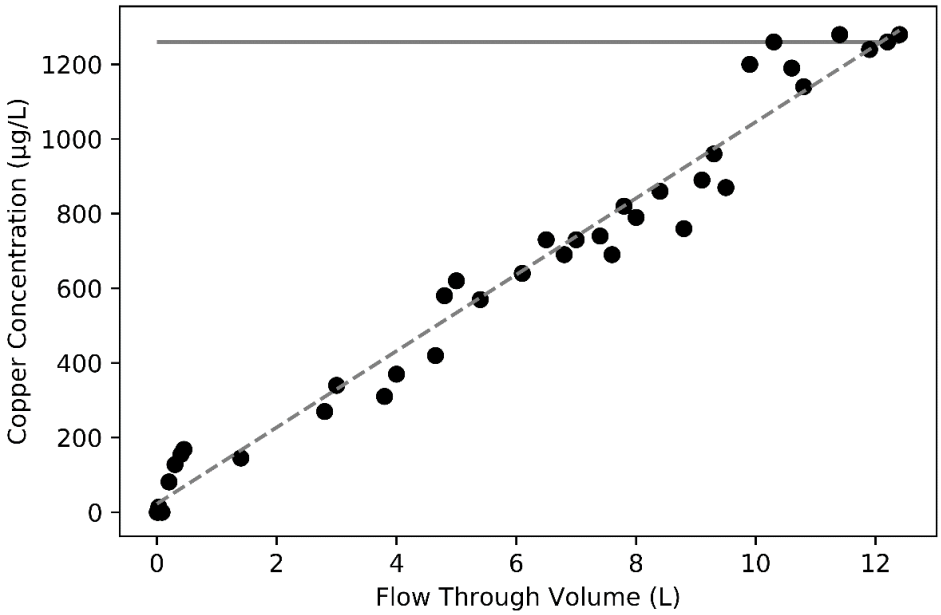

Figure 82. *Copper breakthrough zeolite column (3)*

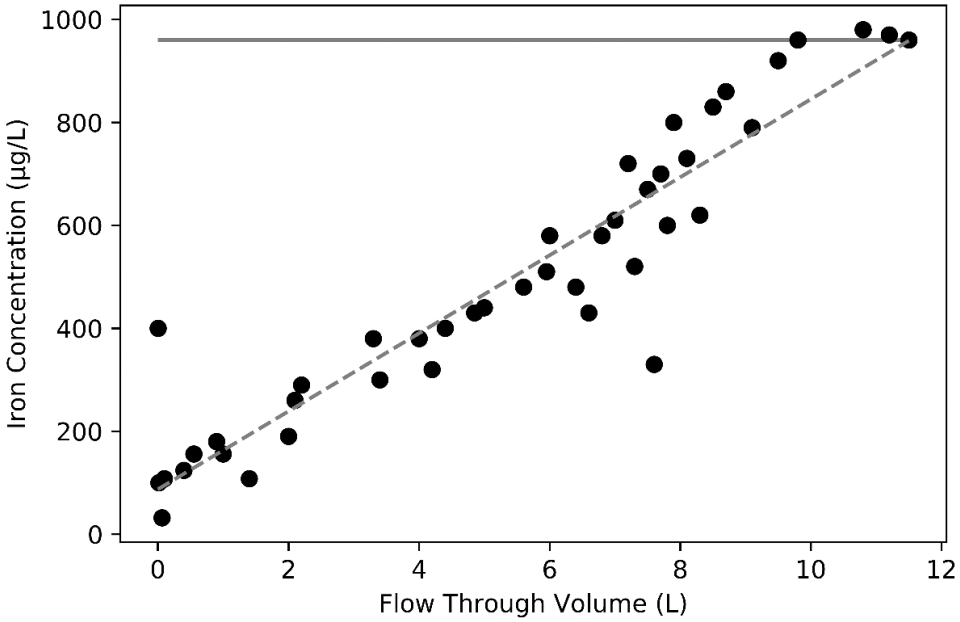

Figure 83. *Iron breakthrough zeolite column (2)*

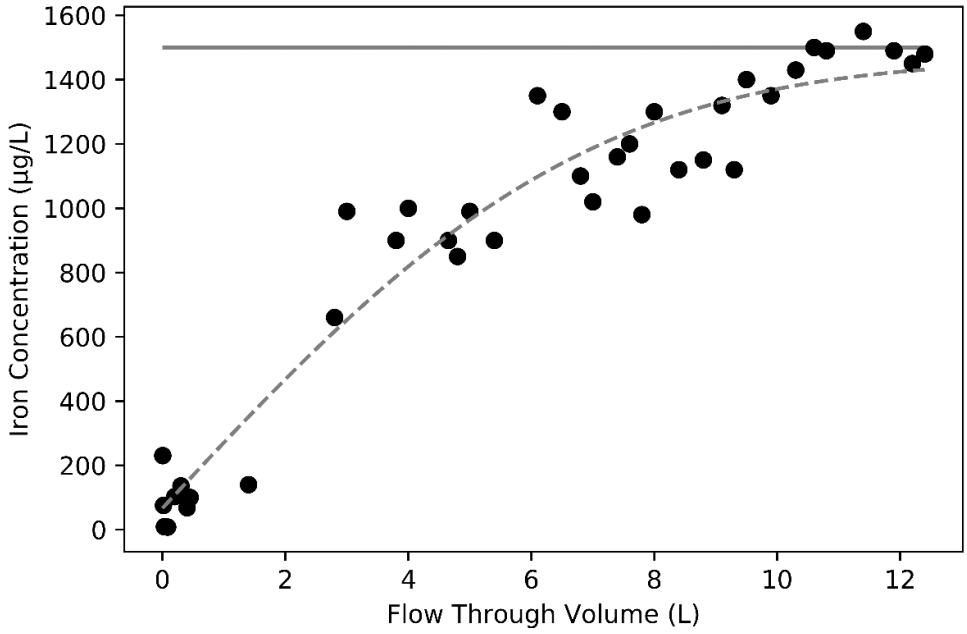

Figure 84. *Iron breakthrough zeolite column (3)*

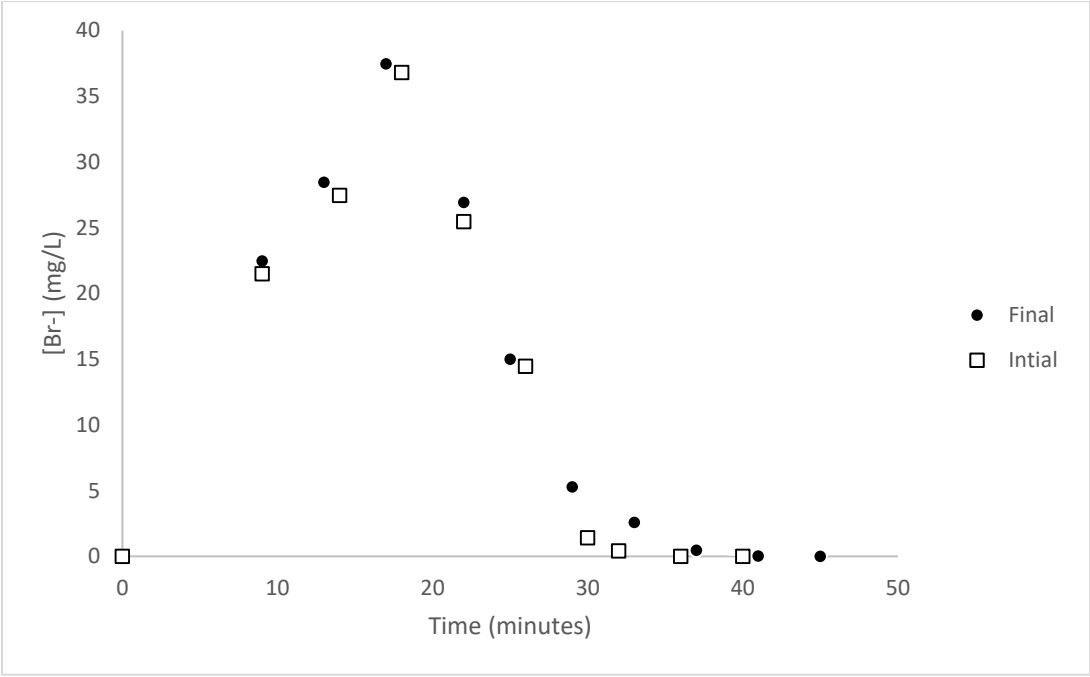

Figure 85. *Sand uninoculated column bromide tracer test results*

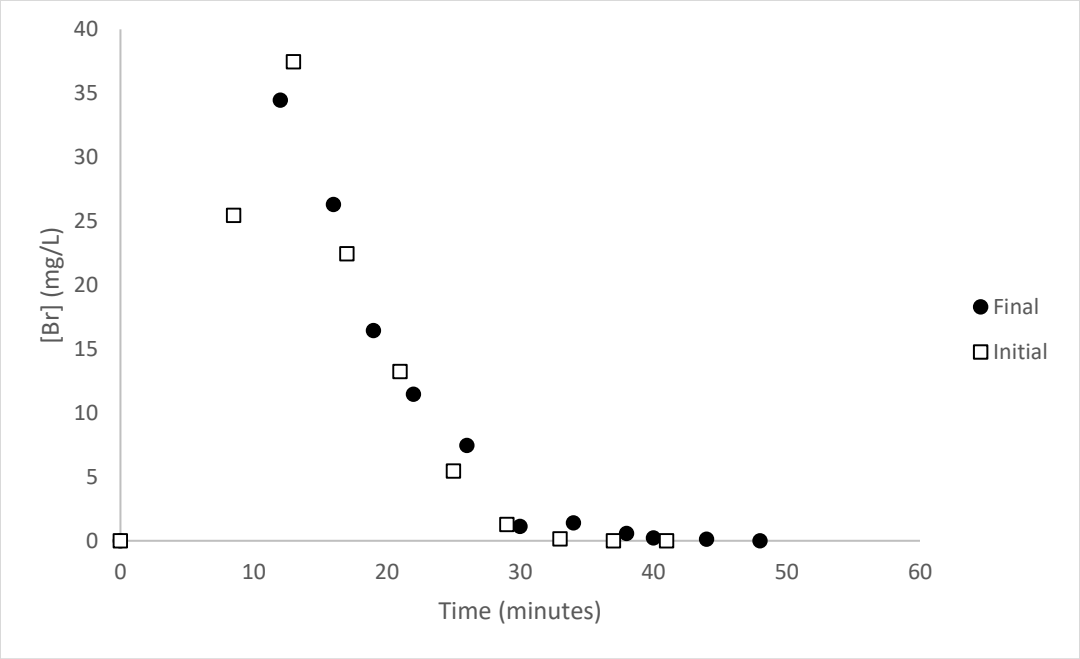

Figure 86. *Marble uninoculated column bromide tracer test result*

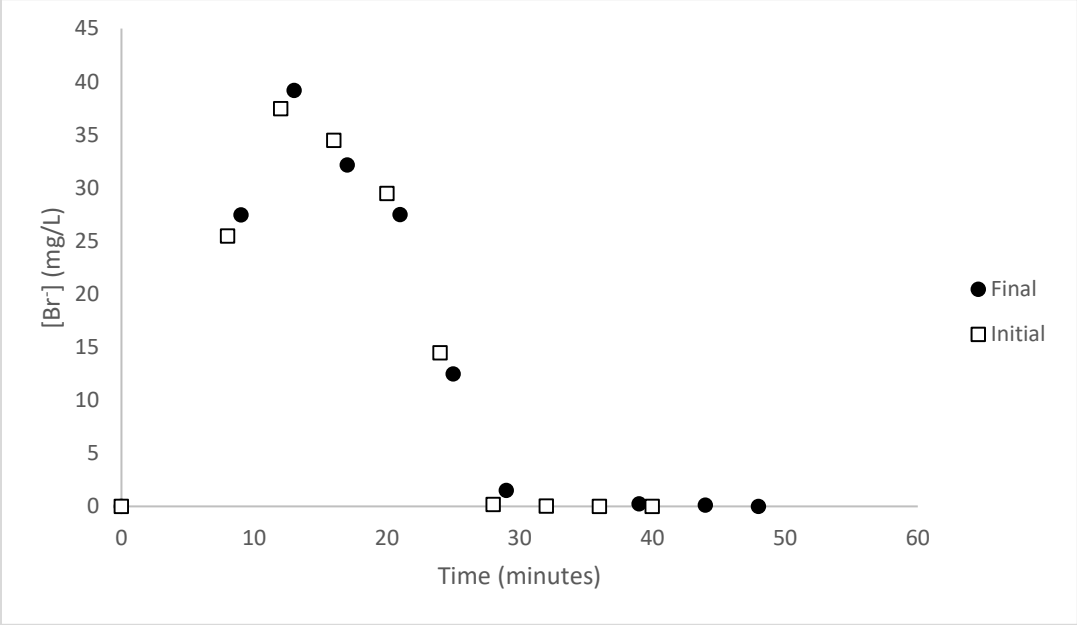

Figure 87. APTsorb uninoculated column bromide tracer test